

Metal Progress

August 1948, Vol. 54, No. 2

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The cover is from a water color by Elizabeth Dwyer and represents a scene in the yard at Midvale Co. (tower over accumulators for press shop in background).

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Mark your answers here. Carbon content of steel A. is ____% B. is ____% C. is ____% Correct spark readings are given at lower left

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C—.95%

B—.35%

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RYERSON STEEL

A Salute to Alloy Steel

By Francis B. Foley

President, ☉
Superintendent of Research
The Midvale Co., Philadelphia

Alloy steel will be the central theme of the 1948 Metal Congress in Philadelphia. In previewing the 30th National Convention, ☉ President Foley invites you to assist in developing the program for "A Salute to Alloy Steel" by suggesting to the committee the names of individuals most deserving to receive the special Distinguished Service Awards for notable contributions to progress in alloy steel (excluding toolsteel, stainless steel, and other highly alloyed ferrous materials).

IT IS FITTING that the attention of all members and friends of the American Society for Metals be called, thus prominently, to the arrangements being made for the 30th National Metal Congress and Exposition (the annual meeting of your Society) to be held in Philadelphia the week of Oct. 25. It is fitting for several reasons.

In the first place, the membership of the Society, recalling a steady progression of successful ☉ Conventions and Expositions, has come to expect a noteworthy event, as a matter of course; yet this fall the national officers have completed preliminary plans for a meeting of special interest, with the theme "A Salute to Alloy Steel". Such a gathering deserves advance publicity.

In the second place, the success of such a Congress and Exposition depends as much — even more — on the *membership* of the ☉ as on the management. The management rightly looks for a notable attendance at the National Metal Congress and Exposition; experience proves that 80% of the membership in the trade area surrounding the convention city will attend, and thousands of members will come from a distance.

However, in one important detail, the Salute to Alloy Steel will be helped greatly by cooperation *in advance* of the members of the American Society for Metals, no matter where they live. I refer to the first of the four special features now being arranged:

1. The selection of candidates from among those in the United States and Canada who have made notable contributions to the progress and development of alloy steels (not including toolsteel, stainless steel, and other highly alloyed ferrous materials), and the preparation of appropriate citations and Distinguished Service Awards.

2. A visualization — by appropriate exhibits on the main stage of the Exposition Building — of the part played by alloy steel in the history and develop-

ment of our country, the progress of alloy steel through engineering, research and technology, and the dependence of the American economy on engineering alloy steel.

3. A program of meritorious technical and historical papers about alloy steel.

4. A symposium of invited papers on the subject "Cold Working of Steel".

These special features, plus the multiple activities always associated with the Metal Exposition, assure a week of truly absorbing interest for those attending the 1948 Convention.

Honorary Committee — Giving testimony to the transcendent importance of alloy steel in the industrial life of the nation, eleven distinguished representatives of American industry have joined with your ☉ President and Vice-President to form an Honorary Committee for the Salute to Alloy Steel. The Committee is listed on the next page. These men from the alloy steel industry and the largest manufacturing industries give added importance to the 30th National Convention by their willingness to participate in this tribute to progress in alloy steel.

Distinguished Service Awards

Another excellent committee has accepted appointment to determine the qualifications of candidates for the Distinguished Service Awards.

Honorary Committee For the Salute to Alloy Steel

Chairman: Francis B. Foley, President, American Society for Metals
William R. Boyd, Jr., President, American Petroleum Institute
A. G. Bryant, President, National Machine Tool Builders' Assoc.
Oliver P. Echols, President, Aircraft Industries Assoc. of America
B. F. Fairless, President, U. S. Steel Corp.
William T. Faricy, President, Assoc. of American Railroads
A. B. Homer, President, Bethlehem Steel Co.
William C. Johnson, President, National Electrical Manufacturers Assoc.
George W. Mason, President, Automobile Manufacturers Assoc.
J. H. Oppenheim, President, Farm Equipment Institute
Walter S. Tower, President, American Iron and Steel Institute
C. M. White, President, Republic Steel Corp.
Harold K. Work, Vice-President, American Society for Metals

On the next page are listed the committee members who will judge the qualifications of candidates whose names are suggested to them.

Here is where the entire membership of the American Society for Metals can help. Let each one of you recall your experiences with alloy steels in the past; compare the early ignorance with present-day knowledge; put down in a letter the names of the people now living who in your opinion really did an outstanding job in making this transformation possible; add what supporting remarks or evidence you think appropriate; and mail the letter to J. M. Schlendorf, Chairman, Distinguished Service Awards Committee, % Republic Steel Corp., Cleveland 1, Ohio.

The Awards Committee will consider nominations of outstanding men in all branches of this great field. But remember that the term "alloy steel" is used in the sense of engineering alloy steel or constructional alloy steel, and is not intended to include toolsteel, stainless steel, magnet alloys, or other highly alloyed ferrous materials that are used for narrowly specialized purposes. The following outline may stimulate your thinking and make it concrete rather than general:

I. Men who discovered, perfected and promoted the metallurgical processes

1. Ferro-alloys and other raw materials used in the melting of alloy steel
2. Equipment and processes for making alloy steel
 - a. Furnaces
 - b. Auxiliaries
 - c. Control equipment
 - d. Refining processes and reagents
 - e. Alloy steel ingot and casting practice
3. Forging and other mill processes adapted especially to alloy steels
4. Heat treating techniques for alloy steels

II. Discoverers of advanced research techniques applicable especially to alloy steel

III. Discoverers of improved techniques of inspection and testing

IV. Discoverers and perfectors of the alloy steels themselves

1. Compositions
2. Control and refinement of microstructure

V. Notable men in the organization and promotion of the alloy steel business

Francis B. Foley, President, and Chairman, Honorary Committee for the Salute to Alloy Steel



VI. Men responsible for notable applications in consuming industries

1. Transportation industries
 - a. Automotive
 - b. Railroad
 - c. Aircraft
 - d. Marine
2. Agricultural machinery
3. Power industries
 - a. Steam
 - b. Electrical
 - c. Gas
 - d. Water
4. Machine industries
5. Chemical industry
6. Petroleum industry
 - a. Drilling
 - b. Refining
7. Civil engineering construction
8. Ordnance

One glance at such an outline should convince you that the Distinguished Service Awards Committee will benefit from the help of all members in order that distinguished work in all branches of the field shall be recognized, without omitting credit where credit is due. Your nominations for recipients of these awards should be sent to Chairman Schlendorf.

J. M. Schlendorf, Vice-President, Republic Steel Corp., and Chairman, "Distinguished Service Awards" Committee



75 Years of Alloy Steel Progress

The President of your Society feels a personal interest in the plans to visualize "75 Years of Alloy Steel Progress", because the first alloy steel used

"Distinguished Service Awards" Committee

Chairman: J. M. Schlendorf, Vice-President, Republic Steel Corp.

Vice-Chairman: Rufus E. Zimmerman, Vice-President, United States Steel Corp.

Robert S. Archer, Vice-President, Climax Molybdenum Co.

John Chipman, Professor of Metallurgy, Massachusetts Institute of Technology

H. J. French, Vice-President, International Nickel Co.

F. P. Gilligan, Secretary-Treasurer, Henry Souther Engineering Co.

W. E. Jominy, Staff Engineer, Engineering Division, Chrysler Corp.

T. W. Lippert, Directing Editor, *The Iron Age*

I. C. Mackie, Director of Metallurgy & Research, Dominion Steel & Coal Corp., Ltd.

Harry W. McQuaid, Consulting Metallurgist

Fred P. Peters, Editor-in-Chief, *Materials & Methods*

Walter E. Remmers, President, Electro Metallurgical Corp.

E. S. Rowland, Research Metallurgical Engineer, Timken Roller Bearing Co.

Earl L. Shaner, Editor-in-Chief, *Steel*

A. E. White, Director, Engineering Research Institute, University of Michigan

Clyde E. Williams, Director, Battelle Memorial Institute

anywhere in the world for an engineering structure was made in the plant of Wm. Butcher Steel Works (predecessor of The Midvale Co.), which occupied portions of our present site in Nicetown, Philadelphia. I refer to the chromium-carbon steel compression members placed in the main arches of the historic Eads bridge over the Mississippi at St. Louis.

It is fitting, therefore, that the coming Philadelphia convention of the American Society for Metals should visualize the 75 years' progress of an idea and an industry born here so long ago. A special committee, under the chairmanship of Robert A. Wheeler, is charged with the responsibility for collecting exhibits that will do this as clearly and dramatically as may be — not only the steelmaking processes but also the machines and other applications that mark the milestones of this journey. The personnel of the committee is an adequate guarantee that its task will be achieved.

Committee to Visualize "75 Years of Alloy Steel Progress"

Chairman	Robert A. Wheeler, Manager of Publicity, Nickel Sales Dept., International Nickel Co.
Aircraft Industry	J. B. Johnson, Chief of Materials Laboratory, Wright-Patterson Air Force Base
Automotive Industry	A. L. Boegehold, Head, Metallurgical Dept., Research Laboratories Division, General Motors Corp.
Electrical Industry	W. E. Ruder, Research Laboratory, Metallurgical Division, General Electric Co.
Farm Equipment	Harry B. Knowlton, Supervisor of Materials Engineering, International Harvester Co.
Machine Tools	Richard F. Harvey, Metallurgist, Brown & Sharpe Manufacturing Co.
Petroleum Industry	Robert W. Schlumpf, Chief Metallurgist, Hughes Tool Co.
Railroads	Ray McBrian, Engineer, Research & Standards, Denver & Rio Grande Western R.R.
Steel Industry	M. A. Grossmann, Director of Research, Carnegie-Illinois Steel Corp. C. H. Herty, Jr., Asst. to Vice-President, Bethlehem Steel Co. E. C. Smith, Chief Metallurgist, Republic Steel Corp.
Display Consultants	R. B. Hanna, Display Dept., General Electric Co. H. H. Harris, President, General Alloys Co. D. C. Miner, Advertising Manager, E. F. Houghton & Co. C. M. Parker, Secretary, Committee on Manufacturing Problems, American Iron & Steel Institute

Advance Registration

One feature of the Metal Exposition that the 350 exhibitors like is the availability of detailed information, both during and after the event, about the character of the attendance. This information does not issue automatically from a calculating machine at the national headquarters. It has to be secured from properly completed registration cards, and in the past many people have been irked by annoying delays at the registration desk, no matter how many clerks may have been present to care for anticipated peaks in the attendance.

Such delays will be avoided, the officers of your Society hope, by the scheme of advance registration. If you will turn to page 273 of this issue of *Metal Progress* you will find a form that you can fill in and mail, and you will have returned to you an entrance badge which will enable you to walk right through the gate!

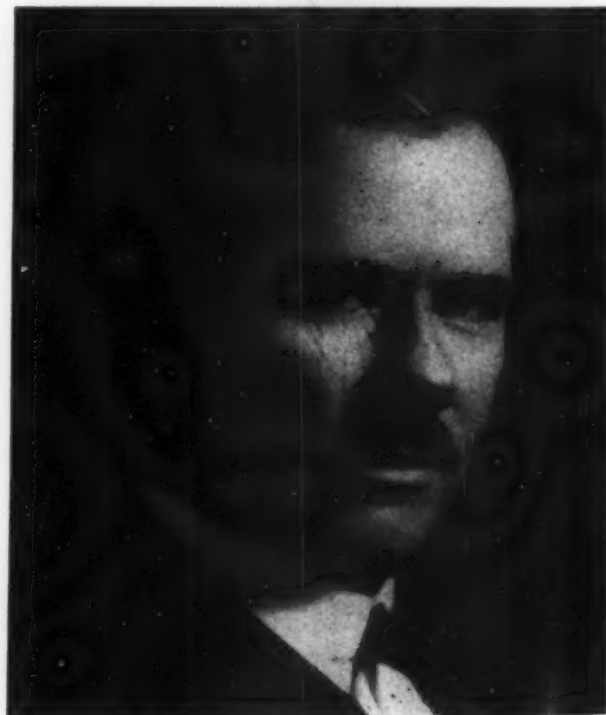
Robert A. Wheeler, Chairman,
Committee to Visualize "75
Years of Alloy Steel Progress"

Technical Program

For 30 years, the American Society for Metals has published technical papers about alloy steel. In fact, through the years, no other subject has been discussed so amply in the *Transactions*. At the 1948 Metal Congress, this record of American progress in alloy steel will be carried forward again, with 19 of the convention papers reporting the latest developments in the science and technology of alloy steel. In addition to the regular technical sessions, there will be a special report dealing with the history of alloy steel in America, and a symposium on the cold working of steel.

Metallographic Exhibit

Another matter deserving advance attention from members of the American Society for Metals is the metallographic exhibit to be held in Convention Hall. This will be the third such exhibit. The rules are few and simple. They are printed on page 240.



Atmospheres

for the Heat Treatment of Steel

By Floyd E. Harris

Furnace Engineer
Buick Motor Division, G. M. Corp.
Flint, Mich.

In this article, the first of two, the author (well known to readers of Metal Progress for his contributions during the past few years on the theory and practice of carburizing) presents a generalized but simplified statement of the commercial atmospheres used for modern heat treatment of steel, the elementary chemistry and physics applying to gas-metal reactions and diffusion of carbon, and a little of the historical background showing how present practice has been achieved after traveling down a long road of development.

A PHYSICAL CHEMIST recently commented that natural phenomena proceed quite independently of our mode of analysis. There are few metallurgical problems where this observation seems more apt than those dealing with atmospheres in the heat treatment of steel. Let us, therefore, analyze a few of these problems in a search for the viewpoints that are the simplest and hence the most instructive. We will generally search for the simplest correlations between the atmosphere's composition and the steel's properties—all the time having due regard to the influence of temperature on both. These correlations must be quantitative. Too often postulates are given involving reactions which are quite limited and relatively unimportant. The question of pertinent data arises, since it is often as important to find *why* a certain result obtains as it is to recognize

the result itself. Thus, a mass of unrelated data may often be quite confusing and misleading. We must treat the roles of atmospheres and steels as parts of a consistent whole, if our exposition is to be effective.

The broad problem divides naturally in two parts or categories. The first involves a careful study of *fundamental principles*. These include the chemical reactions that are possible, the rate at which they proceed, the chemical "potentials", the "catalytic effects" or surface reactions, together with steel properties such as the limits of solubility of carbon and its rate of diffusion. The second and equally important division concerns the *specific process*, and the results desired in a given operation. This latter division includes the actual problems encountered in the plant, and the discussion may well begin with a general

survey of the problems arising when steel is exposed to elevated temperatures.

Natural Atmosphere

The existence of an atmosphere in all heating operations is readily appreciated, even by the casual observer. One visual proof is the temper colors on the surface of polished steel specimens as they are slowly heated. This coloration may be analyzed by measuring the temperature of the specimen and noting the time to acquire a definite blue. If conditions are controlled rather carefully, it is observed that the color for a given temperature after a short holding time may often be duplicated at a somewhat lower temperature if the holding time be increased. Similarly, the color observed as the piece reaches temperature will

gradually deepen with elapsed time up to a certain point, after which the color seems established, and no further change is noted.

In this simple experiment — qualitative though it may be — the effect of the atmosphere of a given composition (that is, the mixture of nitrogen and oxygen found in air) is demonstrated by the formation of an oxide film on the steel surface. If it is agreed, with the physicists, that the color gets deeper as the oxide film gets thicker, it is further demonstrated that the extent of the reaction between iron and oxygen is a function of time and temperature.

An even more common phenomenon involving reaction between polished steel surfaces and their surroundings is found by observations at room temperature: If the air is quite dry — that is, relatively free of water vapor — the formation of rust is slow; days may elapse before any noticeable discoloration appears. However, if water is dropped on the sample so that only portions of the surface are wetted, the rusting reactions are greatly accelerated, and in a few minutes a noticeable discoloration is evidenced on wiping the surface with a clean cloth. If the wetted specimen is heated to a temperature just below the boiling point of water, the reaction is greatly speeded, and under certain conditions the surface is entirely coated in a few seconds. In this event the composition of the atmosphere in contact with the steel is not one of nitrogen and oxygen alone; at the surface (or interface) the air is saturated with water vapor. The amount of water vapor that can be carried by air increases rapidly with temperature, and both the temperature and the water vapor content have a pronounced effect on the iron-oxygen reaction which produces rust.

Prepared Atmospheres

Literally speaking, any gas or mixture of gases surrounding the steel part constitutes an atmosphere. So defined, the illustrations given above are as apt as any of the varied industrial processes with which we will deal later. However, many heating processes cannot be performed in the simple air medium without extensive damage to the material being heated, and the definition of "atmosphere" in this sense implies the *control* of its gaseous composition. For such processes, the parts are heated in chambers where the flow of controlled atmosphere is sufficient to exclude the surrounding air. This heating space containing the atmosphere and the parts is customarily designated in shop parlance as the muffle, the retort, or the work chamber.

Commercial atmospheres are somewhat lim-

ited as to composition (the ingredients themselves) as well as to their relative amounts. Volumes measured in thousands of cubic feet per hour are frequently needed, so prepared gases must be easily made from materials that are readily available, and which are of relatively low cost. In fact, the "base" or "carrier gas" is often produced from common fuel gases and air, under controlled reactions in an auxiliary retort or generator. The total list of gases that may be applied to the work chamber for the processes we are to consider are but eight in number, three of which, oxygen (O_2), nitrogen (N_2), and water vapor (H_2O), have already been mentioned. The completed list includes carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2), methane (CH_4), and ammonia (NH_3). If the two solid elements found in all steels, namely carbon (C) and iron (Fe), are included in the group, the major reactants in our heating processes are found. The number of possible reactions that might be written from these ten components is enormous, and we shall use only a few of them.

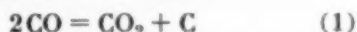
Before any chemical reactions are written, a word of caution seems desirable, since the mere writing of reactions can be very misleading. Let us be ready to interpret or at least to analyze a given reaction when it is quoted. A few examples covering the analysis of pertinent reactions may serve as illustrations.

Reaction Analysis

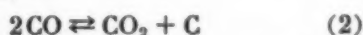
A simple but informative experiment is found in the book by R. Schenck entitled "The Physical Chemistry of Metals", published in English translation in 1908: This German investigator placed a glass tube in a carefully controlled electric furnace maintained at 825° F. The tube was connected to a vacuum pump and it was thoroughly exhausted, and then pure carbon monoxide (CO) fed into the empty tube until its pressure was slightly above the normal atmospheric pressure of 760 mm. of mercury. This tube or work chamber was also connected with a manometer so that the pressure inside could be continuously observed. In this first experiment there was no observable change in pressure as time went on; evidently pure CO is practically stable at 825° F. in a clean glass tube.

Next the experiment was repeated, but with the difference that the evacuated work chamber contained some clean nickel shavings. After the CO had been led in and the feed line closed, the pressure dropped fairly rapidly and within an hour it had reached slightly under 500 mm. of mercury, but then remained constant with time. A slight deposit of sooty carbon was noticed on the nickel.

Evidently the carbon monoxide was decomposing in such a manner that the number of molecules was reduced (the pressure of the gas had dropped, despite constancy of total mass and temperature of the gas), and this reaction had reached completion within an hour. The reaction involved was the reverse of the one commonly known as the "producer gas reaction". It was



Note further that the reaction had not *completely* transformed the CO into CO₂ else the pressure would have dropped to exactly half that at the beginning, to correspond with halving the number of gaseous molecules. Some CO is in balance ("in equilibrium") with the CO₂ and C at 500-mm. pressure and 825° F. This is noted by writing the above equation as



which infers that the relative amounts of CO and CO₂ in equilibrium with C will depend on the temperature and pressure of the mixture.

One further point is important, before we go on to Dr. Schenck's third experiment: The nickel shavings did something like triggering an action that did not occur in the tube without the metal. Examination of the nickel after the experiment showed no change, after the loose carbon was brushed off. Chemists say that nickel "catalyzes" the reaction; it takes part in it without showing any permanent effects. Similar catalytic reactions that deposit unwanted soot have badgered metallurgists in many carburizing processes.

In the third experiment with this equipment, the conditions were duplicated except that iron filings replaced the nickel. The pressure began to decrease immediately, again indicating that CO is decomposing into CO₂ gas and solid carbon. However, the reaction did not stop at 500-mm. pressure, as it did with nickel, but continued to drop although at a constantly decreasing rate. If such an experiment is continued for a long time, the pressure in the container eventually approaches a very low figure. The curves for the two experiments with nickel and iron are given in Fig. 1.

These are extremely suggestive experiments. For the nickel phase, verification is given for the producer gas reaction; the final atmosphere is rich in carbon dioxide, and this gas does not react with nickel at 825° F. For the iron phase, the carbon dioxide, formed on the decomposition of carbon monoxide, reacts in turn with iron to form iron oxide at this temperature. The gaseous product of this reaction is more carbon monoxide, which in turn breaks down to carbon dioxide and free carbon; the cycle repeats until the original gaseous mixture is converted almost completely to solid

carbon and to "solid" oxygen (in the sense of oxygen fixed in the iron oxide).

The above experiments illustrate the caution raised at the outset. Here we start with a pure gas (CO), ordinarily thought of as a "reducing" gas, in contact with steel at a relatively low temperature, far below the carburizing range, and the result is a badly scaled metal and a lot of soot!

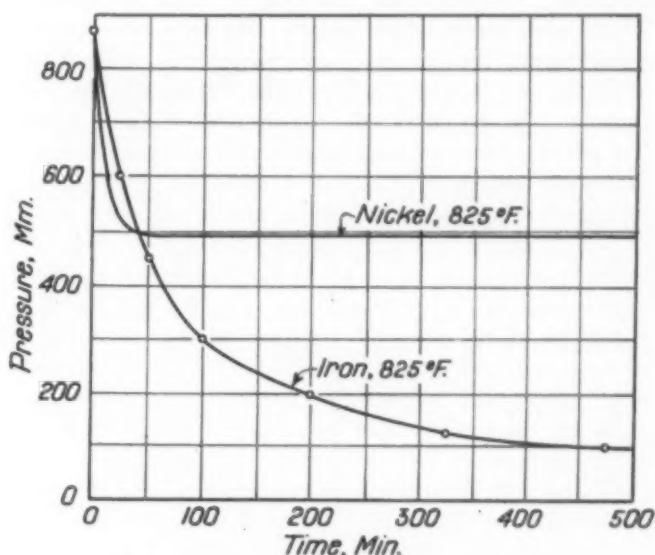


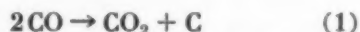
Fig. 1 — Pressure Changes in Closed System at 825° F., Originally Containing Pure CO at 865 Mm. and Metal Filings

Let us extend the analysis, in an endeavor to interpret factors other than chemical reactions. Suppose that an actual process at 825° F. requires the iron surface to be kept clean, or that no oxide be formed. We observe from the curve in Fig. 1 representing the experiment with iron that the rate of reaction slows greatly as the amount of CO remaining in the mixture gets less and less. (The physical chemist would say that the "partial pressure" of CO is decreasing continuously in that experiment.) It would appear logical therefore to compound a gas mixture of a little pure CO in a good deal of an inert gas like nitrogen, and get a mixture that would react very slowly, if at all, with clean steel. We find it difficult and expensive to obtain pure bottled carbon monoxide and nitrogen, but a gas containing 20% CO and the balance nitrogen can be produced in quantity. To counteract the effect of the producer gas reaction, and the damage done to the steel by CO₂ which is so formed, an effluent tube is added to the work chamber, and the pressure in the chamber is maintained by furnishing a continuous flow of the prepared gas. Realizing that the work chamber is at an elevated temperature, and that the density of

gases decreases as the temperature increases, the precaution is taken to maintain the chamber pressure slightly above atmospheric to avoid contamination with any air surrounding the work retort. We may experiment with the size of the opening for the effluent tube; the supply of fresh prepared atmosphere ($\text{CO} + \text{N}_2$) must be sufficient to overcome the rate at which carbon monoxide decomposes, and the tube opening must allow this flow and still maintain the chamber pressure. Under these conditions, the steel surface remains unchanged; that is, no oxide is formed, although a slight amount of carbon will be found in the retort. Yet we find the amount of carbon thus deposited is *less* than though pure carbon monoxide were supplied; thus the dilution with inert nitrogen is actually an advantage to our process!

The above is an excellent illustration of how *dynamics* can be used to keep a reaction within innocuous limits. "Dynamics", of course, involves concepts of motion, gas flow or carbon diffusion, as opposed to the static conditions of equilibrium that are seldom reached in plant operations. Therefore let us pursue the analysis of this reaction between carbon, iron and their oxides further:

The striking phenomena illustrated by Schenck's experiments are not independent of temperature. At 1600°F ., for example, a distinctly different phenomenon is found; in a stream of $\text{CO} + \text{CO}_2$ drawn through hot charcoal and therefore in equilibrium as far as the producer gas reaction is concerned, we find that carbon will be absorbed by the steel—that is, the steel is "carburized". Evidently, the $\text{C}:\text{CO}:\text{CO}_2$ equilibrium at 1600°F . is upset at the surface of the steel, causing the reaction



to proceed, and the carbon is taken into solid solution in the hot iron (austenite) and proceeds to diffuse inward toward regions of lower carbon concentration.

Evidence of this is given in Giolitti's epoch-making book on "The Cementation of Iron and Steel", published in 1915, where the producer gas reaction is analyzed in connection with its ability to furnish carbon to the steel surface. Dr. Giolitti gives a complete critical account of the published work on carburization (one of the earliest metallurgical processes to receive the attention of scientists) up to the time of his more searching experiments, starting in 1907, that proved that the true carburizing mediums are the gaseous compounds of carbon.*

This topic of "the proper interpretation of a

*Using a decidedly improved technique, from an analytical viewpoint, the carburizing reaction of carbon monoxide is further studied by Arthur Bram-

chemical action" should not be concluded without a brief reference to the *oxidizing* properties of the carbonaceous oxides. The student will be well repaid for an examination of the notable paper on "The Chemical Equilibrium Between Iron, Carbon and Oxygen" presented by A. Matsubara before the American Institute of Mining and Metallurgical Engineers, and printed in its *Transactions* for 1922, V. 67, p. 3. Employing carbon monoxide and carbon dioxide in successive experiments, the equilibria for magnetic oxide and for ferrous oxide, termed "the $\text{Fe}_3\text{O}_4\text{-FeO}$ equilibrium" and "the FeO-Fe equilibrium", respectively, are extensively analyzed. Investigation of the carburizing reaction also leads to a diagram showing the relationship for equilibrium between gas composition, temperature, saturated austenite and the oxides of iron at one temperature.

The thermodynamic functions of gases, as determined quite recently with great accuracy from band spectroscopy, are an invaluable aid in the precise analysis of reactions. It might be difficult, however, to find more illuminating references concerning the problems of atmospheres than the works of Schenck, Giolitti and Matsubara, above quoted. They serve as a constant reminder that we must proceed with caution in our interpretations of chemical reactions. Bearing this in mind, let us make a cursory examination of some commercial atmosphere processes. Using a very general division, these may include oxide coatings, clean hardening, and carburizing operations.

Oxide Coatings

Commercial problems involving the designed production of oxide coatings invariably deal with machined or ground steel surfaces. In fact, it is with the finished part, whose surfaces are initially clean, that the major portion of our atmosphere evaluations are directly concerned. Two common

ley and his associates in a series of papers printed in Carnegie Scholarship Memoirs of the Iron and Steel Institute, 1926 to 1928. While it was certain at that time that the active agents in the carburizing process were gaseous carbon compounds, the importance of carbon monoxide in the supply reaction had not been thoroughly analyzed. These British investigators ran a very complete series of laboratory experiments, employing pure carbon monoxide as the gaseous medium. These tests covered a wide range of time cycles, rates of gas flow and temperatures. Curves showing the concentration of carbon at varying distances from the steel surface ("carbon-penetration curves") were obtained by analyzing successive layers of lathe turnings taken from the test specimens, and these results were checked by photomicrographs. From the data, an attempt was made to explain the penetration or diffusion of carbon into steel during carburizing—again, a dynamic process.

practical uses are found for controlling coatings: In the first, the properties of the oxide itself make the process useful; the second use seeks to provide a protective finish. Both processes provide an even and extremely thin coating, although the protective coating is the more tenacious of the two and of lesser depth.

The three oxides of iron in the order of their oxygen content are ferrous oxide, FeO ; magnetic oxide, Fe_3O_4 ; and ferric oxide, Fe_2O_3 . Ferric oxide (Fe_2O_3) is the familiar red rust. At low temperatures it is not generally formed directly, but rather as a decomposition product of ferric hydroxide, $\text{Fe}(\text{OH})_3$. In both of the commercial coatings the formation of ferric oxide (or the hydroxide) is to be avoided. If the parts are initially dry, heating below 700°F . in air forms the superficial oxides or temper colors only. It is between 700 and 1300°F . that the useful oxides are formed; the oxygen content of air is too high to allow any degree of control in the oxide formation in this temperature range; the steel's surface is roughened, and the oxide is often loose or irregular. A prepared atmosphere is essential to the coating process.

The first application uses pure water vapor ("pure" in the sense that it is not contaminated with air) in the latter part of the heating cycle. With parts initially dry, the charge is heated to not over 650°F ., or at least until all parts are over 300°F ., the heating being in the normal air atmosphere. The air is then completely displaced by steam, and this displacement must be completed before any portion of the load reaches 800°F . The steam atmosphere must be maintained, without contamination with air, at least until the steel surfaces are completely covered by the oxide film.

The reaction above 1030°F . is



Below 1030°F . it is

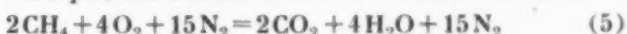


The reactions as written show that below 1030°F . the stable oxide is the magnetic oxide, and above that temperature it is the ferrous oxide.

If the atmosphere be contaminated with air—that is, if the atmosphere is partly water vapor with appreciable amounts of free oxygen—an extremely fast reaction sets in, having ferric hydroxide as a product. The coating is then very soft and free, much like a rust deposit, and is extremely undesirable. The true oxide coating, properly processed, is quite tenacious and seems to be part of the steel itself. Viewed under a high powered microscope, the coating appears quite porous, and this porosity gives it the property of retaining an oil film much better than a finished bare metal surface can. For parts which are sub-

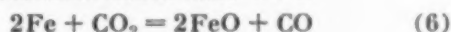
jected in use to a scrubbing or lapping action, the oil film allows the surface to be burnished before the oxide disappears through wear. This coating is also applied to certain classes of tools, and to punches used for extruding sheet metal parts.

For the *protective* oxide coating, the atmosphere is chiefly carbon dioxide. At low temperatures the reaction with iron is less rapid than it is with steam, although identical oxides are formed. The required atmosphere is easily prepared by removing the water vapor from the products of complete combustion as gaseous fuel with air. For example, the combustion of methane and air is



Most of the four volumes of water vapor, symbolized at the right in equation (5), may be eliminated (at least to the dew point representing saturation at the temperature to which the gas is cooled) by spraying the gas with cold water. The final composition of gas cooled to 64°F ., as supplied to the work chamber, is approximately 2% H_2O , 11.5% CO_2 , 86.5% N_2 . This atmosphere, from the application standpoint, has the advantage over steam that it can be in contact with the steel throughout the entire heating range. Treatment in such a gas mixture is particularly suited to a tempering operation following clean hardening. When a quench in soluble oil follows this low-temperature operation, a pleasing surface finish is found, making the process quite desirable for bolts or other threaded parts.

The reaction above 1030°F . is



and below 1030°F .



It is thus seen, by this very brief discussion, that carbon dioxide, the "bad actor" when bright annealing or clean hardening is desired, can be used to advantage when properly controlled as to temperature and moisture content for the production of a colored finish with very desirable properties. Likewise, moisture by itself, also under proper control, can produce another oxidized finish with other specialized properties.

Since carbon monoxide, carbon dioxide and moisture are the universal constituents of flue gas or of partially burned fuel gas (the common source of economic atmospheres for commercial applications) it is necessary that we know the properties of these gases, either alone or in combination, as functions of temperature and pressure. This will lead us into the subjects of clean hardening and a more precise consideration of gas carburizing—matters which will be taken up in the second portion of this article, to appear in *Metal Progress* next month. ●

High Speed Photographs of

Made by Robert A. Buchanan

Research Laboratory
U.S. Steel Corp.
Kearny, N. J.

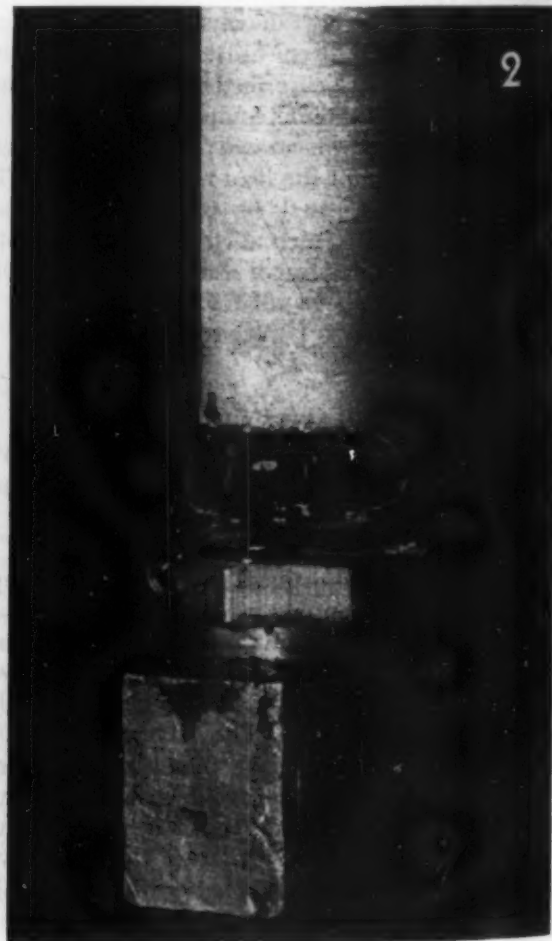
THIS series of five stroboscopic photographs shows the initial stages in end-quenching a red hot bar of steel with a jet of water in the standardized manner. The entire period covered is but a fraction of a second, the exposure in each case being 1/10,000 sec. The source of illumination, which was placed about 2 ft. from the bar, was one gas-filled tube through which was passed an electrical discharge from a condenser. This discharge was set off manually on the judgment of the photographer. The camera was a 4x5-in. Speed Graphic with the lens at f22. Super-XX film was used.

The action, which is far too fast for the eye, is "stopped" so that one may study in detail the behavior

of the stream of water as it makes contact with the hot steel surface.

The first photograph is reminiscent of some of the photographs of the early stages of the burst of the atomic bomb in the first New Mexico test. The second shows the water just as it makes contact with the surface of the steel at which there appears to be some turbulence. In both the first and second photographs, the reflection of the discharge tube in the water is plainly visible.

The last three photographs show how the mushroom of water forms and how it appears to rise above the edge of the steel bar. Picture No. 5, which is taken at closer range, illustrates how small particles are thrown off at the edge of the steel. These are assumed to be tiny drops of water, though they might be particles of scale. ●



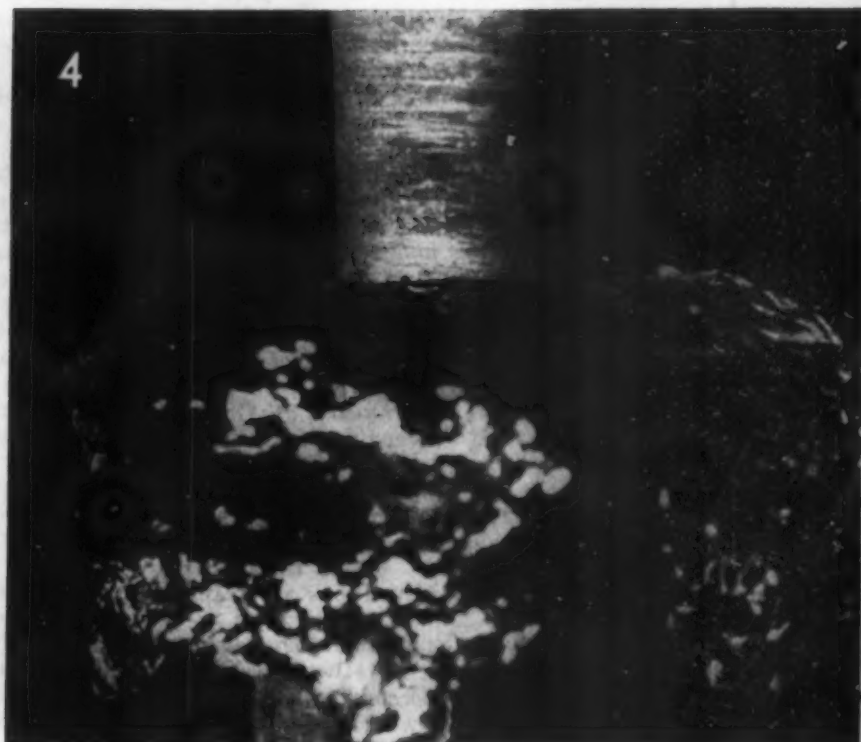
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Water Jet in the End-Quench Test

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Training and Research in Atomic Energy

IN *Metal Progress* for April certain American developments in atomic energy were indicated by quotations from the third semiannual report to Congress of the United States Atomic Energy Commission. Especially, these included general plans for the expanded production of fissionable materials and for the design and construction of more efficient reactors and energy generators. A major fraction of the report describes research facilities and a research policy designed to utilize the full scientific potential of the nation. The cooperative programs of training and research in the national laboratories are briefed in the following verbatim extracts:

An inseparable part of the Commission's responsibility for the development of atomic energy relates to the training of men who will do the work. The three national laboratories at Chicago, Oak Ridge (Tenn.), and Patchogue (Long Island), with their total of 52 associated universities, are important training as well as research centers. The broad base of participation in atomic energy research by academic institutions is in itself important from an educational standpoint. All of the research programs at educational institutions are training programs as well.

The Clinton National Laboratory* at Oak Ridge is an outgrowth of the huge wartime development in the production of fissionable materials at this location. Cooperating with the Clinton National Laboratory are 14 southern universities, combined, under charter from the State of Tennessee, into the Oak Ridge Institute of Nuclear Studies. It is under contract to the Commission for extensive research and training. The 14 participating institutions are Alabama Polytechnic, Catholic University, Duke, Emory, Georgia Tech, Louisiana State, Tulane, Alabama, Kentucky, North Carolina, Tennessee, Texas, Virginia and Vanderbilt Universities.

The Oak Ridge Institute has developed several programs. The graduate training program permits selected graduate students from various universities to complete their thesis research with work at Oak Ridge; during the fall semester 198 students registered for courses. A supplementary graduate training program enables regular employees of the local operating contractor to continue work while studying subjects required for their theses at Oak Ridge instead of going elsewhere. The school of nuclear science of the Institute provides advanced study at the post-doctorate level in special problems related to nuclear reactor development. The research participation program will make it possible for scientific staff members of educational institutions to take part in the research programs of the operating contractors. Also, the Institute will conduct a special school in radioactive tracer techniques, beginning in the summer of 1948.

Argonne National Laboratory is successor to

the "Metallurgical Laboratory" established early in the war at the University of Chicago. It is still operated for the Atomic Energy Commission by the University, and the following 29 participating mid-west institutions are represented on the Council: Battelle Memorial Institute, Carnegie Tech, Case Tech, Illinois Tech, Indiana, Iowa State, Kansas State, Loyola (Chicago), Mayo Foundation, Michigan Tech, Michigan State, Northwestern, Missouri, Nebraska, Pittsburgh, Notre Dame, Ohio State, Oklahoma A. & M., Purdue, St. Louis, Chicago, Cincinnati, Illinois, Iowa, Michigan, Minnesota, Wisconsin, Washington (St. Louis) and Western Reserve Universities. The laboratory, now scattered over the campus of the University of Chicago, is to be consolidated at a single Government site. Land is being acquired in Du Page County, and designs are under way.

Brookhaven National Laboratory at Patchogue, Long Island, was established to enlist the scientific cooperation of the great educational institutions of the Northeast. It is operated by Associated Universities, Inc., a corporation formed by the following nine universities: Columbia, Cornell, Harvard, Johns Hopkins, M.I.T., Princeton, Pennsylvania, Rochester and Yale. A major purpose of the laboratory is to provide exceptional facilities to young scientists for training in nuclear research. Although Brookhaven neither awards degrees nor grants academic credit, selected graduate students are permitted to carry out their doctorate investigations, using its special facilities.

During 1947 a fellowship program was developed in the Division of Biology and Medicine of the Atomic Energy Commission. This program is designed to train qualified persons for careers in the medical and biological aspects of atomic energy. For this purpose the Commission has budgeted approximately \$1,000,000 for the first year. A similar plan for research fellowships in the physical sciences is under development.

Basic research [under authorization and financing by the Commission] was expanded during 1947 in the fields of physics, chemistry and metallurgy. This work includes the metallurgy of both fuel elements and reactor working materials. The principal facilities where basic work on atomic energy is under way are: Argonne, Battelle Memorial Institute, Brookhaven, Oak Ridge, Columbia University, Ames Laboratory (A.E.C., at Iowa State College), Massachusetts Institute of Technology, California, the National Bureau of Standards, [Los Alamos Scientific Laboratory (A.E.C.), Hanford Directed Operations (A.E.C., at Richland, Wash.) and Knolls Atomic Power Laboratory (A.E.C., at Schenectady)].

*Now known as Oak Ridge National Laboratory ("X-10" in local parlance), operated by Carbide & Carbon Chemicals Corp., contractor to the Atomic Energy Commission.

Presentation of verbatim extracts from important contemporary documents concerning atomic energy does not imply that the Editor agrees with the opinions quoted, nor that they are expressions of A.S.M. policy.

A Simple, Accurate Microhardness Testing Device

By E. Boerje Bergsman

Chief Metallurgist
Munkfors Works
Uddeholm Co., Sweden

This apparatus, a wartime development in Europe, uses an inverted metallographic microscope, whereby the exact location of the spot to be tested can be fixed. The objective is then replaced by another holder in which a pyramidal diamond is accurately centered, and specimen is lowered onto the diamond's point. A counterbalanced lever system regulates the pressure between diamond and specimen (the indenting load) between limits of 0.5 and 500 g., and the resulting impression is measured by micrometer eyepiece in the usual manner. Several routine laboratory investigations made with this equipment are described.

is used as an indenter, the hardness number is obtained by measuring the diagonals of the impression, and is expressed as the test load per unit area of the impression in kg. per sq.mm., according to the formula:

$$H_{VP} = \frac{1854 \cdot P}{d^2}$$

where H_{VP} = the Vickers number in kg. per sq.mm.

P = the load in g.

d = the length of the diagonals of the impression in 0.001 mm.

In order to obtain reliable results, the preparation of the samples, the testing itself, and the measurement of the impressions must all be carried out in a standardized manner, adhering to certain rules. As these are a question of pure routine, microhardness tests can be left to the more qualified laboratory assistants when the necessary instructions have once been given, and after a certain amount of practice they can be

carried out almost as quickly as an ordinary Vickers test. It is necessary to employ a microscope having the best possible resolving power in order that the dimensions of the indentation may be precisely determined.

To attain the utmost precision in static indentation tests, it is important that the diamond be as perfectly shaped as possible and the apparatus be free from any vibration. The loading speed should be kept constant during a series of comparative tests, and the load should remain applied for a sufficient time to insure a static condition. A loading speed of 1 mm. per min. and a 15-sec. duration of loading have proved suitable.

The experiments which have been carried out in Sweden indicate that the Vickers numbers

MICROHARDNESS testers described in the literature are based either on the scratch method, or on the method of static indentation. In a scratch test the cutting instrument, usually a diamond point, is drawn with constant pressure across the surface of the specimen instead of being pressed at right angles against it. In the method of static indentation the indenter is pressed under a known load and for a certain time into the material. In microtesting, the indenter is usually a diamond pyramid with a vertex angle of 136° , and its direction of movement is at right angles to the surface of the specimen.

When a hardness number based on an absolute scale is required, the static indentation method is nearly always employed. If a Vickers diamond

obtained by microhardness testing can be regarded as "normal" Vickers numbers. If necessary, therefore, the tables already available for converting the normal Vickers or the microhardness scale to another (like the Rockwell C-scale or the Brinell numbers) can be employed with satisfactory accuracy, which is certainly of importance from a practical viewpoint.

Method of Testing

The applications to be described have all been carried out in the laboratory of the Munkfors Works of the Uddeholm Co., Sweden, with a microhardness tester designed and constructed under the author's supervision, and obtainable from the company's American offices.

The tester differs from other microhardness testers principally because of the facts that the necessary load is applied direct to the specimen (thus simplifying the construction) and that the specimen instead of the indenter is movable.

The apparatus, shown mounted on the stage of a metallographic microscope in Fig. 1, can be used with any standard inverted microscope with only slight modifications necessary to suit various types of stage and objective holder. The indentation is made with a Vickers diamond, fixed in a holder which is interchangeable with the microscope objective. The diamond can be centered in this holder so that the indenter's point can be brought in line accurately with the optical axis of the objective.

Static indentation tests for quantitative measurements are made in the following manner:

The specimen is placed in the holder with the polished surface to be tested facing downwards, and is fastened with a screw clamp. The clamp is inserted into a bayonet mount in the holder.

The weight disk is now applied and, after balancing with the adjustable counterweights, the desired weight (that is, the indentation load) is applied.

The specimen is adjusted so that the area to be tested is located at the cross-wires. The microscope objective is then replaced by the indenter holder, wherein the diamond has already been centered.

The test area and diamond point are then brought in contact by lowering the specimen stage with the coarse adjusting screw, proceeding with the fine adjusting screw when the diamond nearly touches the specimen. At the moment when the diamond point lifts the specimen and its holder, an electric circuit is broken and a small lamp is extinguished. The indentation load is then functioning, and the diamond makes an impression in the specimen.

After a suitable length of time the specimen stage is raised and the diamond holder is replaced by an objective for examining and measuring the impressions. (Alternatively, a whole series of spaced

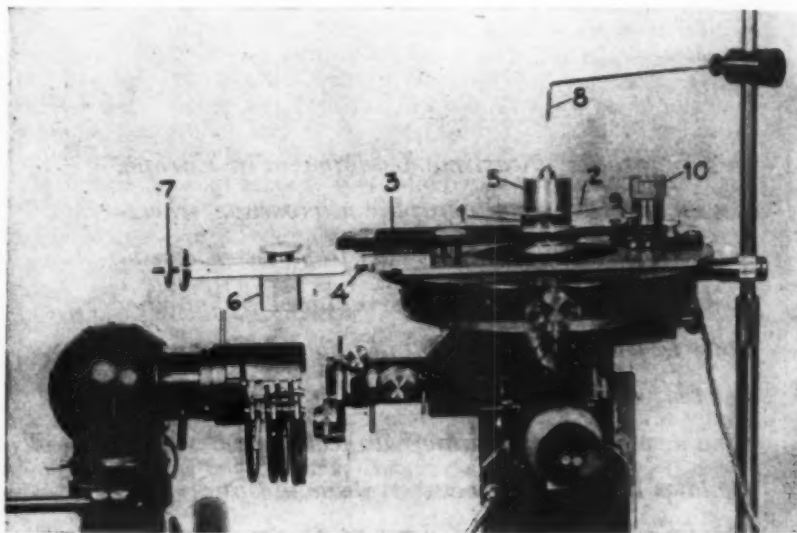


Fig. 1 — Bergsman's Microhardness Tester Mounted on an Inverted Microscope

(1) Specimen holder, (2) weight disk, (3) lever, (4) axle, (5) indentation load — fixed interchangeable weight — which is placed on the weight disk after counterbalancing by the adjustable counterweights (6) and (7), (8) indicating pointer for adjusting weight to correct position centered above the diamond point, (9) electric contact broken when diamond point lifts the specimen and its holder, (10) electric lamp showing when contact (9) is broken.

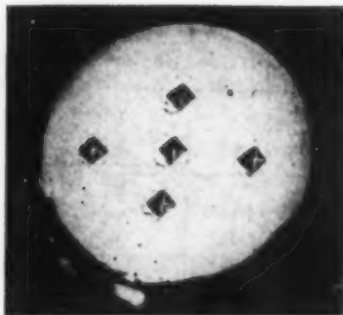
indentations can be made consecutively by moving the specimen stage.)

Measuring the impression's diagonals is best done by an eyepiece screw-micrometer. Although slightly less accurate, an ordinary eyepiece micrometer can be used. The average of the two diagonals is then used for computing hardness by formula.

Typical Applications

The instrument can easily be used for making scratch tests employing loads of 0.5 to 5 g. In these tests the specimen stage is lowered and then moved in the desired direction.

Fig. 2—Impressions $\times 350$ in the Cross Section of a Wire, 0.10 Mm. (0.004 In.) Diameter. Indentation load: 50 g. Vickers hardness: 750 kg. per sq.mm.



The wide range of utility for microhardness testing can be illustrated by the following examples, which have been chosen primarily as applications to purely practical questions. Microhardness tests can also throw light upon many research problems of more or less theoretical interest; examples, however, have not been included in this paper.

It is sometimes necessary to determine the quality of a material from a very small sample only. For example, a wire, 0.10 mm. (0.004 in.) in diameter, was tested without difficulty on a cross section mounted in bakelite for polishing, as shown in Fig. 2. Other similar applications are the determination of hardness of the working surface of small dental drills, thin twist drills, metal fragments, and file teeth.

Another special problem is the testing of foils



Fig. 3—Impressions $\times 1000$ on 0.013-Mm. (0.0005-In.) Aluminum Foil. Indentation load: 1 g. Vickers hardness: 26 kg. per sq.mm.

for hardness. If the testing conditions are such that the depth of the impression is small in relation to the thickness of the foil, the correct hardness number can be obtained even on thin and soft foils. For example, Fig. 3 shows some impressions made in an aluminum foil, 0.013 mm. (0.0005 in.) thick,

with an indentation load of 1 g.

The hardness of thin surfaces, such as electrodeposited layers, can also be determined. A few results are given in Table I.

As can be seen, the indentation load has been chosen to give an impression whose diagonal is less than the thickness of the coating. As the depth of the impression is

Table I—Hardness of Some Electroplates

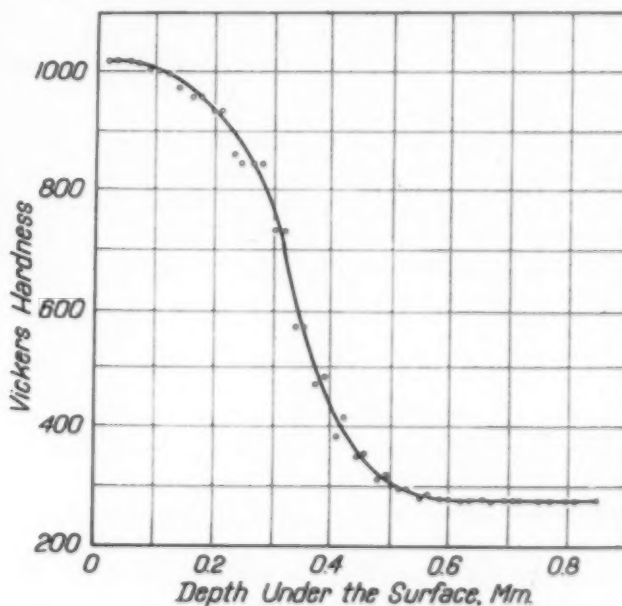
COATING	THICKNESS		LOAD	DIAGONAL	VICKERS HARDNESS
	MM.	IN.			
Chromium	0.010	0.0004	25 g.	0.0068 mm.	1000
Nickel	0.010	0.0004	10	0.0074	339
Zinc	0.015	0.0006	5	0.0113	73
Silver	0.030	0.0012	25	0.0205	110

only one-seventh of the diagonal, it is obvious that there is no danger of piercing the layer and so obtaining a false hardness number.

Carburization, decarburization and nitriding are instances of some important industrial diffusion processes. Figures 4 and 5 illustrate the possibilities of measuring the extent of the diffusion zone by microhardness.

In Fig. 4 numerous microhardness tests were made on a cross section of a piece of nitrided steel, 10 mm. (0.394 in.) square. Impressions were

Fig. 4—Hardness Penetration in the Surface Layer of a Nitrided Steel. Indentation load: 100 g.



placed in line at an oblique angle to the surface, thus enabling the investigator to make a more detailed study of the hardness variation, since a larger number of impressions can be placed within the surface layer under examination.

Good results can also be obtained by using a section cut at an acute angle to the surface.

By combining the two methods — that is, by making the impressions on a taper-ground surface along a line at an oblique angle to the surface boundary, hard-

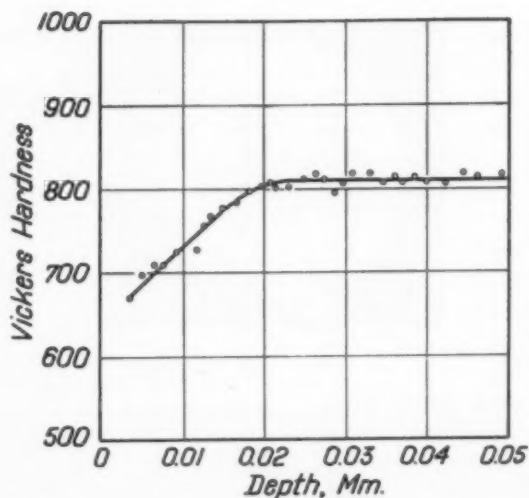


Fig. 5 — Hardness Curve Showing the Possibilities of a Detailed Study of a Very Thin Surface Layer (600 Readings per Mm.)

grains in the structure, provided these are larger in cross section than 0.005 to 0.010 mm. (0.0002 to 0.0004 in.). This limitation in size is mainly due to the fact that the resolving power of the best metallurgical microscope cannot be carried further than about 0.0003 mm. (0.00001 in.); with small impressions, therefore, the error in measuring will be disproportionately large. When testing very small grains of a microstructure, it is of importance that the indenter be faultless right

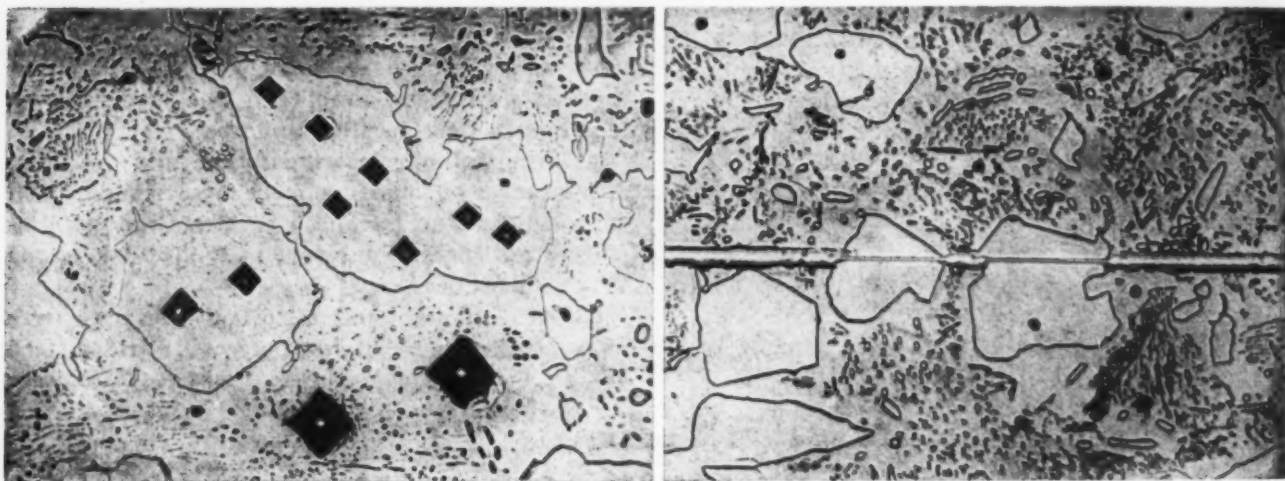


Fig. 6 and 7 — Hardness of Chromium-Iron Alloy (0.70% C, 22% Cr) Tested by Indentation and Scratch, Respectively. Ferrite is 215 hard, chromium carbide 1060. Indentation load: 25 g. Scratch load: 2 g. Magnifications: 650 and 500×

ness variations can be studied even in very thin layers. The diagram in Fig. 5 shows an instance where 31 impressions were made in a surface layer only 0.05 mm. (0.002 in.) thick. This corresponds to about 600 readings per mm. (approximately 16,000 readings per in.).

Hardness of Microscopic Components

The characteristics, including hardness, of multiple-phase metals depend on the properties of the constituents. An ordinary hardness test represents the average of the alloy on account of the large area covered by the impression.

A microhardness test, however, enables the investigator to determine the hardness of individual

up to its very point, which often is not true. Quite naturally, also, the precision of aim decreases as the size of the grain in question becomes smaller. Furthermore, the impressions must be considerably smaller than the grain being tested in order that the hardness of surrounding or underlying material will not influence the result.

Figure 6 shows massive chromium carbide in a ferritic steel with 0.7% carbon and 22% chromium. The Vickers hardness of the carbide is 1060, and of the adjoining ferrite 215. Figure 7 shows a scratch test on the same material.

Figure 8 shows a high speed steel with 0.7% C, 18% W, 4.5% Cr, and 0.7% V. The hardness of the tungsten carbide, 1800 Vickers, is more than twice that of fairly hard martensite (800 Vickers).

The frame of scratches in Fig. 8 has been made in order to locate the testing area readily. The scratch on the right, leading off the picture, goes right out to the edge of the specimen. After locating this scratch, which is very simple, it is only a matter of following it to the frame which encloses the impressions.

Both Fig. 6 and 8 show the precision of aim which a trained operator can reach with this simple and accurate testing equipment. The larger carbide

ness tests in the joint itself, hardness numbers up to 420 Vickers were recorded, which were unexpectedly high for the low-carbon material in question. This high hardness could be explained by the fact that the heat was conducted away quickly by the water-cooled copper electrodes, and at the same time the carbon content was a little on the high side. By lowering the carbon content a softer joint was obtained; likewise the weld showed a satisfactory quality.

Brittle Material

Attempting to determine the hardness of brittle materials by the ordinary macro methods will result in fractures. By using a sufficiently small indentation load, however, satisfactory hardness impressions can be obtained. This is well illustrated in Fig. 9 by a series of impressions in a brittle iron aluminide layer. This layer was formed in the following manner: After cleaning in molten flux the iron was dipped in molten aluminum whereby a very brittle layer was formed. When testing, several large cracks appeared around the 200-g. impression, at the right. Around the 100-g. impression there are three cracks, and each 50-g. impression has one crack. When using a 25-g. load and lower, impressions without any cracks can be obtained in this fragile material, 770 Vickers hard.

Cracks around an impression (and consequently a hardness number which is too low) have also been noticed when testing hardened, untem-

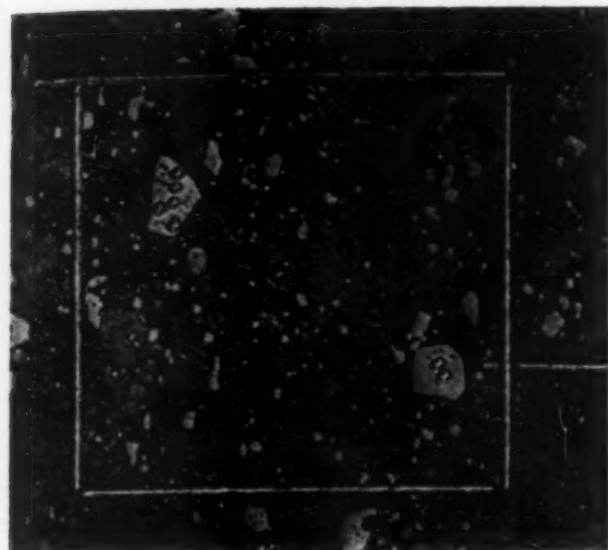


Fig. 8 — Vickers Test on High Speed Steel. Indentation load: 25 g. Vickers hardness: martensite 800, tungsten carbides 1800

particle in Fig. 8, in which five impressions have been made, has a length of 0.027 mm. (0.0011 in.) and a width of only 0.015 mm. (0.0006 in.). The length of the sides of the square frame is 0.13 mm. (0.005 in.) — that is, the same as the thickness of a safety razor blade.

Another common problem is to determine the hardness variation in welded joints.

One examination made in the author's laboratory was carried out on a very poor pressure weld of soft carbon steel. The joint seemed as if it were glued instead of welded. By means of microhard-

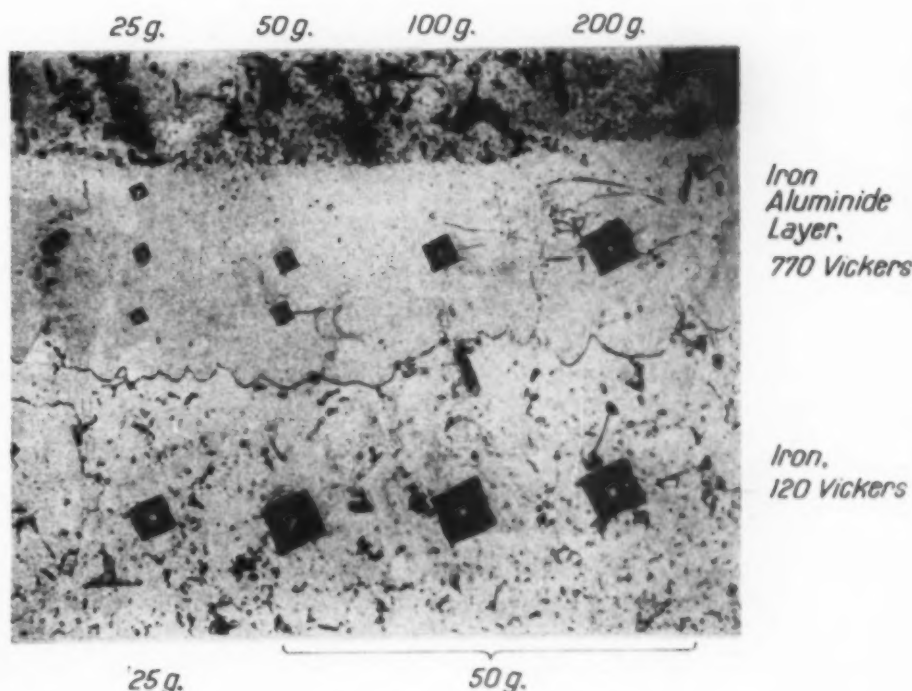


Fig. 9 — The Surface Layer $\times 350$ on a Dip-Aluminized Iron. Not heat treated

pered steel if too great a load is used. By testing with smaller loads, impressions without any cracks can be made and correct hardness numbers obtained.

Hardness Changes Caused by Cold Work

When deep drawing articles such as cartridge cases or cooking utensils, hardness variations are caused by different degrees of cold work in different areas. This hardness distribution can be studied in great detail by microhardness testing, and a clear picture obtained of the stress distribution caused by drawing.

Cold stamping similarly increases the hardness, but it is generally localized. Nevertheless, it can be of some practical consequence. This was

found when examining a hardened and tempered saw whose teeth had been punched from the blade rather than cut or ground. Due to an unsatisfactory die, excessive burr was caused. A microhardness test showed a definite hardness increase of about 50 Vickers numbers near the edge. As a result, a greater amount of filing was necessary than if a better die causing a less amount of cold work had been used.

In summary, it may be said that this simple device for microhardness testing can be used by any first class laboratory technician, once he has been trained in the routine. Several practical applications of the test have been described, including the study of surface layers, cold work patterns, foils, very small metallic objects, and even microconstituents.

Correspondence

Crucible Furnaces for Nonferrous Melting

PITTSBURGH, PA.

To the Readers of METAL PROGRESS:

The article "Brass Foundry Practice at Crane Co." by H. M. St. John (*Metal Progress*, October 1947) contained one illustration that may be misleading—Fig. 8, described as "Advanced Type of Brass Melting Furnace; Crane Co.'s Design as of 1915".*

These furnaces are of unique construction. No installation of this type was ever made in any other foundry. Modern crucible furnaces used for melting nonferrous metals in the foundry include many improvements, notably (a) better mechanical design; (b) improved refractory linings, (c) more efficient insulation, (d) adaptation to all commercial sources of energy, and (e) greatly improved crucibles.

The recent improvements in crucible furnaces have resulted in low labor costs, improved

*EDITOR'S NOTE: The wording of the caption was unfortunate. It was intended to state that in 1915 this was an advanced type of furnace. Continued use of these furnaces for more than 30 years indicates that the design was sound.

working conditions, fast melting, and easy control of metal quality. The following tabulation shows the expansion that took place in the crucible melting method during recent years:

YEAR	FOUNDRIES	CRUCIBLE FURNACES	CAPACITY, LB. PER CHARGE
1942	2,455	9,633	2,693,704
1946	2,771	13,891	4,976,305

An example of stationary crucible furnaces melting 250 lb. of red brass in 30 min., using 1000-B.t.u. gas, is shown on the opposite page.

RICHARD H. STONE
Sales Manager
Vesuvius Crucible Co.

Low-Temperature Creep of Steel

PARIS, FRANCE

To the Readers of METAL PROGRESS:

The creep of steel at high temperatures has been studied extensively during the past 25 years, but creep has seldom been measured below the recrystallization temperature of the steel in question. Actually, creep can be observed at temperatures far below the recrystallization temperature, and even as low as room temperature.

A few results concerning low-temperature creep were published in 1943 by Pomp in Germany. More recently de Strycker, of the University of Louvain (Belgium), has studied the problem in connection with the use of prestressed concrete beams in which steel reinforcing wires are subjected to a tension of about 140,000 psi. so that the concrete is under compression. Depending on composition, drawing schedule and diameter, the tensile strength of these wires varies from 170,000 to more than 350,000 psi., and the elastic limit from 140,000 to 280,000 psi.

When such wires are subjected for a long time to a stress of about two thirds the tensile strength, there are definite indications of creep. The stress at which these deformations are first perceptible is extremely variable and cannot be stated as a definite fraction of the tensile strength or the elastic limit. Sometimes this fraction is as low as 25% of the elastic limit, and sometimes it exceeds 50% of the elastic limit. The shapes of the creep curves for two steels under equal load (for example, 60% of the tensile strength or 75% of the elastic limit) can be different, even when the two steels have the same composition, fabricating schedule and diameter.

It is therefore quite impossible to judge the behavior of these materials except by creep tests on the particular steel or alloy to be used. If it is necessary to predict the behavior of a material precisely, long-time tests are required. Definite indications can be obtained in a week, although 24-hr. tests can be used to make a pre-

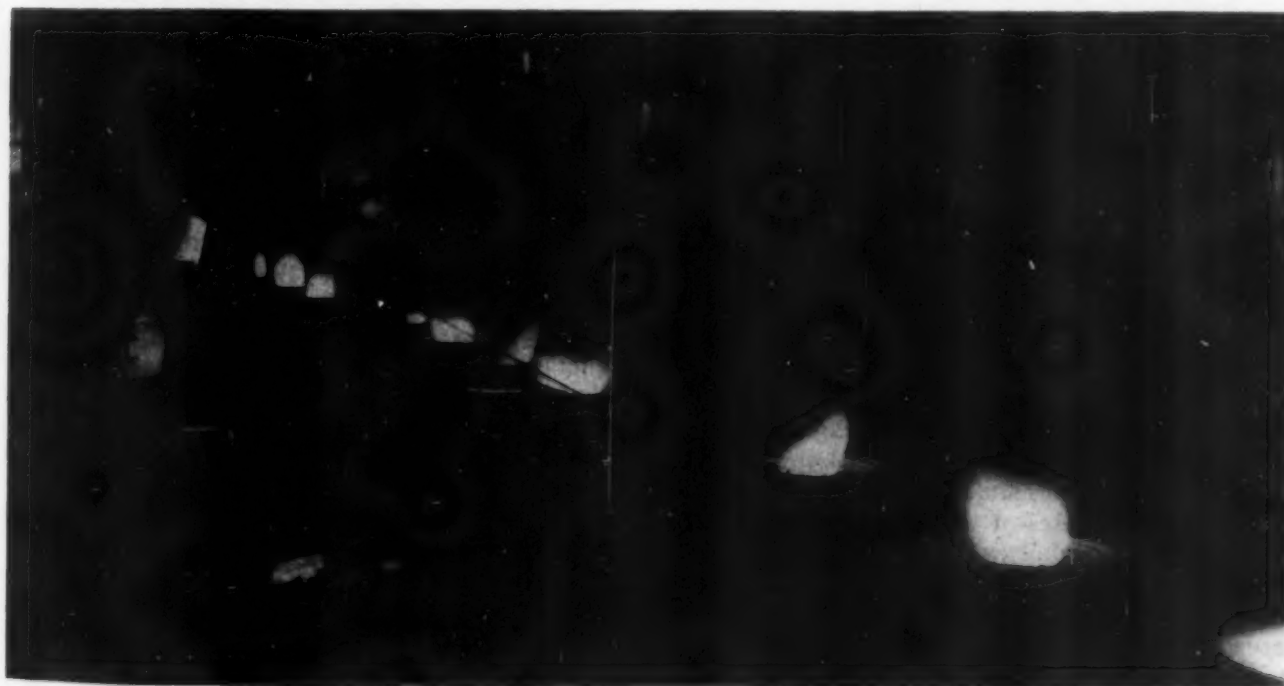
liminary selection among steels produced according to different schedules.

Measurements of low-temperature creep are delicate. A precision of one part in a million is necessary in determining elongations. Mechanical extensometers are not suitable, since they cannot be adapted readily to the large gage lengths (often in excess of 20 in.) that are required in order to obtain the desired precision. Optical extensometers can be used, but it is necessary to take every precaution to avoid errors caused by variations in temperature. In particular, the extensometer should have the same coefficient of thermal expansion as the specimen being studied. De Strycker has adopted a base length of 200 mm. (7.874 in.) and has measured the length by optical means to one twentieth of a micron.

Creep can be expressed in terms of relaxation, and it is sometimes preferable to substitute relaxation tests (in which stress is measured under constant elongation) for creep tests (in which strain is measured under constant load). But it is no easier to predict the behavior of a material from relaxation data than from creep data.

Low-temperature creep is complex but it merits close and systematic examination. A committee for the study of this subject has been organized in Belgium, under the auspices of the Institute of Scientific Research for Industry and Agriculture. The committee includes representatives of steel mills, wire mills, contractors, mechanical industries and university laboratories.

ALBERT PORTEVIN



Metallurgy and Its Place in Engineering Education

By John Chipman
Professor of Metallurgy
Massachusetts Institute of Technology
Cambridge, Mass.

Many colleges have recently added metallurgical courses. The older-established courses in metallurgical engineering vary considerably in content, depending on their historical origins and the interdepartmental relationships in the college in question. It results that there is no standard curriculum — perhaps just as well. The present paper (an abridgment of an address before the American Society for Engineering Education) attempts to outline the field of modern metallurgy, and describes the courses of study set at Massachusetts Institute of Technology after prolonged discussion with metallurgists of widely differing backgrounds.

METALLURGY is the science and art of extracting metals from their ores, refining them, and preparing them for use." Webster's definition seems perfectly acceptable in a broad sense although its conciseness demands amplification. Metallurgy is indeed a *science* and one of the oldest. Modern metallurgy includes the science of the metallic state, of the structures and properties of metals and their chemical and physical nature and behavior.

Metallurgy is an *art* in that it involves the skill and ability to produce and employ metals, the systematic application of the knowledge of individuals and of organizations in the adaptation of metals to the uses of man.

In short, metallurgy is engineering.

This dual nature of metallurgy requires that its students be trained in both science and engineering, a requirement which is not at all unusual in modern engineering education. It has led also

to the present rather anomalous situation in the metallurgical profession that a large fraction of the older members received their basic schooling in other fields.

The term "metallurgical engineering" if used in the broadest sense means exactly the same thing as "metallurgy", but for purposes of the present discussion I shall use the latter as the broader term to include metallurgical engineering and the science of metals. The outline on the following page attempts to set forth the principal features of the entire field of metallurgy, not as a curriculum but as a field of human endeavor. (It is of course impossible to divide any science sharply into cells; the boundaries are inevitably blurred and the divisions overlapping. Nor is it feasible to show in simple outline the

interrelationships between the several branches and their relations to other fields of science and engineering.)

It is hoped that the outline will not be interpreted as an attempt to divide the field into petty domains or to classify all metallurgists as either scientists or engineers. Rather it seems to me a clear demonstration that a well-rounded metallurgist must be both engineer and scientist and that a well-balanced curriculum must contain widely diverse elements. Lacking any universally accepted terminology or scheme of classification, some terms will be defined as we go along, at least as to their scope.

A Curriculum in Metallurgy — An outline of a field cannot serve as an outline of a curriculum. Its usefulness lies in what help the educator may derive from it in perspective and balance. Other factors must also be weighted heavily — local conditions, availability of staff, student needs. Many

acceptable solutions are possible and many of the controlling factors are not visible in the outline.

Some of these pertinent facts which were considered important in developing the curriculum at M.I.T. were the following: (a) The great majority of graduates go into the industries, whereas perhaps 12% take graduate work; the curriculum must serve both groups. (b) Few of the students know at the outset what kind of metallurgical industry they will enter; alumni records show wide diversity in fields of work. (c) There are no dominant metallurgical industries nearby and no concerted demand for specialization.

The outline contains very much more material than can be packed into a four-year curriculum. We cannot hope to train a student in physics and chemistry and metallurgy and several kinds of engineering without making his education exceedingly thin in many spots. We accepted the practical limitation of a four-year course for the great majority of engineering students, and wondered how much of our outline could be included.

Since much must be omitted, it was agreed at the outset to concentrate upon *principles* and omit descriptive material except when it was needed to avoid confusion. In this respect our task of framing a curriculum was simplified by the thoroughness of instruction in mathematics, physics, and chemistry throughout the first two years in all our engineering courses. In these courses the freshmen and sophomores not only study the calculus and differential equations but also use them in everyday problems. Add to these a year of physical chemistry and a semester of crystallography and mineralogy and the apparent total of basic science in the curriculum is 38% — actually this represents only the fraction which is taught in science departments of our institution, because much of the material in metallurgy could be accurately classed as basic science, as will be shown presently.

So much has been written recently regarding the importance of sociological and humanistic studies to engineers that I shall merely record agreement with those who attach high importance to them. In our curriculum the time allotted is 17%, and this must include English, history, economics and a number of elective subjects such as labor relations, fine arts, international relations, or history of ideas.

Instruction by members of other engineering

An Outline of Metallurgy

METALLURGICAL ENGINEERING	METALLURGICAL SCIENCE
I — Mineral Dressing 1. Comminution of ores 2. Separation of minerals 3. Leaching II — Process Metallurgy 1. Roasting and sintering 2. Reduction and smelting 3. Fuels and combustion 4. Heat and fluid flow 5. Electrometallurgy 6. Melting, refining and alloying 7. Casting and solidification III — Metal Processing 1. Hot and cold forming 2. Foundry practice 3. Joining 4. Surface treatment 5. Powder metallurgy 6. Heat treatment IV — Application Metallurgy 1. Selection and specification 2. Alloy design 3. Quality control 4. Service behavior	I — Chemical Metallurgy 1. Crystal chemistry and mineralogy 2. Thermodynamics of systems and processes 3. Reaction kinetics 4. Surface chemistry 5. Corrosion and electrochemistry II — Physical Metallurgy II-a. Metallography 1. Structure of alloys 2. Equilibria in metallic systems 3. Recrystallization and grain growth 4. Reactions in the solid state II-b. The Physics of Metals 5. Atomic and electronic structure 6. Diffusion 7. Electrical and magnetic properties 8. Theory of the solid state II-c. Mechanical Metallurgy 9. Elastic and anelastic behavior 10. Plastic flow and fracture

faculties includes graphics, statics, and dynamics, strength of materials, heat measurements, machine tool laboratory, and the fundamentals of electrical engineering. The remaining 32% of the program is available for metallurgical subjects and electives.

Metallurgical Engineering

Let us now discuss briefly the main subdivisions in the left-hand column of the Outline.

Mineral dressing is the preparation from the ore, as it comes from the mine, of concentrates suitable for smelting or other processes of metal production. It includes such unit operations as crushing, grinding, conveying, flotation, and the separation of minerals by magnetic and gravitational methods as well as by their aerodynamic or hydrodynamic behavior. As generally taught from the standpoint of basic principles and unit operations, it certainly warrants a semester course in any metallurgy curriculum. Laboratory work may include the quantitative study of such operations as comminution, classification, magnetic separation, flotation, filtration and an introduction to the microscopy of ores and the surface chemistry of minerals. One of the dominant thoughts in shap-

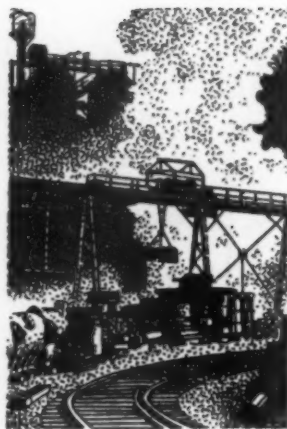
ing our present curriculum was the recognition of mineral engineering as a field of sufficient importance in many geographical regions to warrant a curriculum of its own. The one-term course mentioned serves as an introduction to the field for both metallurgical and mineral engineering students.

Process Metallurgy — Instruction in process metallurgy has undergone considerable development and its importance warrants further careful planning of courses. The older type of descriptive course began with the ore and described with the aid of drawings and photographs the equipment and processes used all along the line to produce an ingot or slab of usable metal. Such courses have been superseded by more quantitative ones having the emphasis on principles and accompanied by problems.

There has never been a sound reason for separate elementary courses in ferrous and non-ferrous metallurgy, nor have there been profitable results from such separation. What is needed is a straight-forward engineering approach to the problems of metal production, and the model for this approach is already available in the field of chemical engineering.

Most methods used in the production of metals can be analyzed in terms of a small number of unit processes. Moreover, these are based upon certain principles which are more or less common to all processes, chemical and metallurgical. The curriculum must rely upon courses in physics, physical chemistry and thermodynamics for most of the *scientific* principles involved; the *engineering* principles must be taught as a part of process metallurgy. This will include such subjects as stoichiometry, heat balances, fuels and combustion, flow of fluids and flow of heat, refractories and furnaces, and instrumentation. The approach to these principles must be quantitative, with the solution of problems playing an important part in the educational process. In our curriculum this course in principles comes in the second half of the junior year.

Some of the unit processes of metallurgy may be mentioned for illustration, without attempting a complete listing. These include gas-solid reactions, such as those occurring in roasting or reduction and blast furnace smelting; gas-liquid reactions as in converting; electrolysis as in refining. These processes as well as the principles underlying them form suitable subjects for laboratory study. For this purpose small equipment designed to illustrate principles and to make quan-



titative measurement is preferable to large and more expensive apparatus designed in imitation of plant equipment. In our curriculum the laboratory work accompanies the study of unit processes in the first half of the senior year. It follows junior courses in physical chemistry and in the principles of metallurgical engineering.

In registering opposition to "descriptive" courses I do not wish to imply that process metallurgy courses should be entirely devoid of description. The student needs a framework upon which to fasten his knowledge of unit processes. He needs specific examples to which he may apply the principles he is studying. It is the *emphasis* which is important; so long as the emphasis is on fundamental principles and their quantitative application to metallurgy the amount and choice of supporting descriptive material can be determined on the basis of local interest or individual preference. In this matter summer employment in industry is of very real value to the student, as well as guided visits to metallurgical plants during the junior and senior years.

As a final course in process metallurgy we are planning a study of flow sheets, integrated plants and operating problems. This should afford opportunity for the teacher to assist the student in bringing to focus the various elements he has been studying separately and, we may hope, will lead in the direction of development of judgment.

Metal processing lends itself so well to laboratory instruction that there is always danger of lapsing into a shop course. The techniques of forming metals into useful shapes are very interesting to the student and hold his attention. To ram a green-sand mold and produce a nice casting in it, to weld two pieces together and find that the weld is strong, gives a feeling of mastery over the metal which is full compensation for the hours spent in developing the skill. But development of skill cannot be even a secondary objective, although it will be a valuable byproduct for many students. Instruction in this field as in others must emphasize *principles*. It should preferably come when the student is also studying physical metallurgy and has had at least a semester of this subject; he can then be expected to examine metallographically the product of his handiwork and to acquire an appreciation for the metallurgical requirements and limitations inherent in the various methods of fabrication.

Application Metallurgy — As the fourth phase of metallurgical engineering we have the task of

putting the right metal in the right spot. This calls forth from the metallurgist all that he has learned in other fields of study; he needs to have an understanding of how metals are made, of their constitution and properties, of how they may be formed and heat treated, and how they will behave in service. This introduces such subjects as fatigue and corrosion and wear; of machinability and weldability and drawability and a dozen other important characteristics. It points up the needs for better metals, for new alloys for special purposes, and is intimately concerned with the writing of specifications and with the economics of metal selection. It embraces also that very important activity, quality control, which seeks to prevent metal failures in fabrication or in service and to make metals reliable engineering materials.

Obviously, much of this knowledge comes only with years of experience. In preparation for this a course in applied physical metallurgy in the final term of the senior year gives the student an insight into the behavior of metals in service. Laboratory work includes practice in the recognition of the metal by microscopic examination, and diagnosis of its condition and suitability for use. Examination of numerous specimens which have failed in service, deduction of the causes of failure and prescription for cure evoke a thorough review of past training and provide an introduction to one of the important professional activities of the metallurgist.

The great importance of economics in metallurgical engineering is not displayed in the outline, nor is it evident in the curriculum established by us. In practice, of course, *any* field of engineering is dominated by considerations of cost and service. Economics, production costs and quality, and the service life of metal structures are matters which require more than casual mention at numerous points throughout the sequence of metallurgical engineering courses.

Metallurgical Science

A large part of the field of metallurgy is applied physical chemistry. Two thirds of the chemical elements are metals and their behavior in the free or alloyed state is of primary importance to the metallurgist. The many reactions involved in the reduction and refining of metals constitute an important part of chemical metallurgy. Corrosion plays a dominant role in the service behavior of many metals and its study (particularly in relation to the structure of the metal) constitutes an important overlapping field of physical, chemical and metallurgical research. Chemical phenomena too numerous to mention

point to the dependence of metallurgy upon physical chemistry.

As far as the second item in the right-hand column of our Outline is concerned, it seems that each field of science or engineering has developed its own special system of teaching thermodynamics. For metallurgical students this can be patterned in part along the lines of chemical thermodynamics, with data and problems drawn from the metallurgical field. In addition, such physical phenomena as order-disorder in alloys, and transformations in the solid state, have made the teaching of thermodynamics a matter of some importance. The time for such a course is after a general course in physical chemistry.

Physical metallurgy is the offspring of physical chemistry and the physics of the metallic state. It is based on an understanding of solid solutions, of phase changes, of diffusion and reactions in the solid state, of equilibrium as summarized in the phase rule, and of metastable states in heat treated alloys. Its techniques embrace microscopy, X-ray diffraction, dilatometry, thermal and magnetic analysis, the measurement of physical properties, and all the varied methods of metallography and heat treatment.

The objective of the science is a complete understanding of the structure and properties of all metals and alloys. It is not sufficient to know *what* happens to an alloy under a given set of conditions. We must begin to formulate an answer as to *why* it happens; it is only in this way that we shall learn to predict the properties of new and untried combinations. Such studies obviously must be given a high place in any metallurgy curriculum, for they contain the scientific bases not only for the future progress of metallurgy as a science but also for the present important function of putting the right metal in the right spot for a given engineering purpose. At Massachusetts Institute of Technology, instruction in physical metallurgy begins with the junior year. It includes metallographic laboratory work in which the student learns to use the microscope, to prepare his own metallographic specimens and photographs, to conduct heat treatments, to follow the course of the reactions in alloys and to interpret these in terms of structure and properties. He constructs a phase diagram from his own laboratory data, and learns to use such diagrams as guides to the heat treatment, structure and properties of alloys. He cold rolls a piece of brass progressively to a fraction of its original thickness, then anneals the resultant pieces, measuring hardness and tensile properties after each step; he records in photomicrographs the successive changes in structure and relates these to the properties of the metal.

In many such experiments he learns at first hand the principles underlying the behavior of metals and alloys. The instruction in this subject throughout the junior year partakes of the nature of a scientific course; engineering applications are reserved for the senior course in applied physical metallurgy.

X-ray methods have become such an important part of both chemical and physical metallurgy that we have developed a separate one-term course for the first half of the senior year. Laboratory work uses as many kinds of equipment as are available, both for radiography and diffraction. The student learns to make radiographs and evaluate them in terms of internal defects. Of greater importance, he learns to prepare samples of metals and nonmetals for diffraction study, to obtain his own diffraction patterns, and to interpret these in terms of crystal structures, lattice parameters, residual strains, and orientation texture.

Professional Elective Subjects

In the courses that have been described in the foregoing paragraphs there has been little opportunity for specialized or advanced study. Attention has been devoted almost exclusively to gaining an understanding, rather than to imparting information. Such a curriculum is open to the charge of being too theoretical, a criticism which could be accepted as high praise.

Some students will inevitably want specialized instruction in some field of applied metallurgy, and this can be met by elective subjects in the senior year. Electives need not all be on applied subjects nor indeed in metallurgy. Some of such courses include electrochemistry, steelmaking, mechanical metallurgy, corrosion, foundry engineering, welding, powder metallurgy, ceramics, the physics of metals (this last being almost a "required elective" for any student primarily interested in physical metallurgy). Many students elect courses outside the field of metallurgy, frequently in the science departments, but occasionally also in the humanities and in business and engineering administration. The time allotted to elective subjects constitutes about one fourth of the total schedule in the senior year.

Thesis—One of the very important features of a senior year is the writing of a thesis and the carrying out of a laboratory study on which the thesis is based. Much can be said in support of the educational advantages of such a properly directed undergraduate activity. It is rare that it will contribute substantially to scientific knowledge; its value lies almost entirely in the training and experience of the student. The fact that the

answer is not known in advance adds zest to the enterprise and should afford a bond of common interest between student and instructor. The field of metallurgy abounds in suitable subjects for such theses, and occasionally the explorer is rewarded by a gem of new knowledge.

Postgraduate Training

It is not a purpose of this paper to discuss graduate work in metallurgy. (It should be remarked in passing that metallurgical research has become an exceedingly active field and that several graduate schools have fairly large enrollments in metallurgy.) For the great majority of graduates in metallurgy who do not continue for an advanced degree, further training must be obtained in the metallurgical industries after graduation. Many industries regularly conduct postgraduate training courses for their younger technical employees. Such courses can be made to fill a real need and to pay big dividends through improved efficiency and a broader understanding of the industry among its younger engineers, salesmen and executives.

The modern scheme of engineering education is becoming more and more dependent upon such training, and both the universities and the industries are according greater recognition to the responsibilities of the latter in the training of engineers. It is neither possible nor desirable to teach a student in college how to operate an open-hearth furnace or a strip mill or what alloy to specify for each part of an airplane. Such detailed knowledge must be acquired in industry. It is the function of undergraduate education to afford the man such preparation that he may profit from industrial experience and thus begin to develop the characteristics of maturity and sound judgment.

[**EDITOR'S NOTE**—The Advisory Committee on Metallurgical Education of the American Society for Metals—of which Dr. Chipman is a member—has recently published a very attractive 96-page booklet "Your Career in the Metallurgical Profession". It is written for the high school senior. It attempts to answer such questions as: "What's metallurgy?" "What is the training required?" "Where is this training available?" "What are the pay-scales at the outset?" "What are the opportunities for advancement?" "How long does it take to get somewhere?"

Distribution of several thousand copies has already been made to faculty advisors in principal high schools and private schools throughout the United States and Canada, and to similar advisors in the 61 colleges which offer metallurgical courses. Any member can get a copy of the booklet for a young man of his acquaintance who is contemplating a metallurgical career (or who should be) by sending \$1 to Society headquarters in Cleveland.]

Composition and Properties of the Natural Oxide Film on Aluminum

By Fred Keller

Chief of Metallography Division

and Junius D. Edwards

Assistant Director of Research

Aluminum Research Laboratories

New Kensington, Pa.

It is important to know as much as possible about the films that form naturally on aluminum because the unusual corrosion and weathering resistance of the metal and its alloys undoubtedly is closely related to this thin and often transparent coating. It presents an effective barrier to oxygen and water, and to many chemical solutions.

THE formation of the natural oxide film on aluminum was described in the first section of this paper on "Behavior of Oxide Films on Aluminum" prepared for the International Conference on Surface Reactions in Pittsburgh in June. The film starts to form as soon as a fresh metallic surface is exposed; in moist air at ordinary temperatures it continues to grow for several days—even months. It is very thin; its thickness will vary from about 10 Å up to 10 times that amount. At temperatures of about 600° C. (1110° F.) the film may reach 1000 Å thick. The composition of these films and their properties will now occupy our attention.

Any such investigation presents many difficulties, particularly when these films are of the order of 100 Å or less in thickness. There is, however, general agreement that, as far as can be determined by X-ray and electron diffraction methods, the films formed in air indoors are generally amorphous. These films have been generally referred to in this discussion as aluminum oxide.

There are, however, certain crystalline forms in which aluminum oxide occurs and which can be identified by their X-ray patterns; the oxide is also

known in several hydrated forms. Table I presents a summary of some of the physical properties of these various forms of alumina and alumina hydrate. (The Greek letter designations of the hydrates are as used in Vol. I of "The Aluminum Industry"; other designations have been used by some authors.)

Gamma-alumina is an intermediate form of oxide produced by heating amorphous alumina or one of the hydrates at a temperature between 500 and 900° C. (930 and 1650° F.). Harrington and Nelson⁹ report that they found evidence of it on thin films of aluminum made by the evaporation technique when these films were heated above 500° C. It has also been observed that anodic films formed on aluminum at a potential of 100 volts or higher contain gamma-

alumina which can be detected by X-ray diffraction methods. Thus it appears that even at room temperature the alumina film under certain suitable conditions tends to assume the crystalline form which identifies it as gamma-alumina. Alpha-alumina or corundum, however, is formed only in air at temperatures above 1000° C. (1830° F.).

In the table, two hydrated forms of alumina are listed. Each of these may occur in two different crystalline forms, alpha and beta.

While the air-formed film on aluminum is generally amorphous alumina (or sometimes gamma-alumina when heated to a high enough temperature), the film formed on aluminum after extended exposure to the outdoors atmosphere is also generally amorphous. When aluminum stands in water the corrosion product is usually beta-trihydrate, although when the water is held at a temperature of 70 to 100° C. the alpha-monohydrate tends to form on the metal.

It has been known for some time that anodic

⁹"An Electron Diffraction Study of Anodic Films", by R. A. Harrington and H. R. Nelson. *Transactions, American Institute of Mining and Metallurgical Engineers*, V. 137, 1940, p. 62.

coatings treated with hot water at 80° C. or higher contain alumina alpha-monohydrate. Harrington⁹ showed that sheet aluminum, not anodized, acquired a film of alpha-monohydrate when heated in water at 80° C. or higher, but not when heated at 60° C. Hydrated aluminas, heated sufficiently to drive off combined water, acquire a porous structure which greatly increases their adsorptive capacity.

Gas Adsorption by Oxide Film

The natural oxide film formed indoors has an appreciable adsorptive capacity, especially with regard to water vapor. When exposed to the weather, substantially thicker and more adsorptive films may be formed. This is being recognized generally and references to this characteristic appear in the literature. Thus, the presence or absence of adsorbed substances must be taken into account in any investigation because of their effects on the behavior of these oxide films.

The matter of gas adsorption by aluminum oxide films was investigated by one of us at Aluminum Research Laboratories about 25 years ago. In this early investigation (unpublished), samples of cast and wrought aluminum that had been exposed indoors were heated in a current of dry nitrogen and the liberated water vapor and carbon dioxide were determined gravimetrically after adsorption in suitable reagents. The hydrogen that was evolved was burned to water and determined in the same manner. These amounts of gas were too small to attach much quantitative significance to the results, but the various experiments showed a consistent trend and warranted the following conclusions:

The principal gas adsorbed by the oxide film was water vapor. When the samples were heated below 300° C. (575° F.), a major portion of the water was liberated as such. At temperatures above 300° C., however, the water vapor appeared to be more firmly held and a greater portion reacted with the aluminum to form aluminum oxide and hydro-

gen. Only small amounts of carbon dioxide were found in the evolved gas.

Using more sensitive techniques for gas collection and analysis, P. T. Stroup further explored this field later in the same laboratories. In his experiments, the test pieces were sealed in a Pyrex glass tube evacuated to 0.01 to 0.1 mm. of mercury, and allowed to stand for 30 min. to insure absence of leaks. Then the samples were heated in an induction furnace. The water vapor evolved was condensed in a U-tube cooled by a mixture of solid carbon dioxide and ether. Other gases were collected with a Töpler pump and were analyzed by microanalytical techniques. The amount of water was determined by subliming it into a calibrated capillary tube. The metal finally reached a temperature of about 600° C. (1110° F.).

By blank determinations, it was found that small but somewhat variable amounts of water were liberated from the Pyrex glass tube. Some of this water might also have reacted with the aluminum to form some of the hydrogen. Because of the indeterminate nature of the blank, however, no correction was made to the observed amounts of liberated water and gas. It is not felt that particular significance should be attached to measured amounts of water plus hydrogen of less than 2.0 ml. per 1000 sq.cm. of surface.

The results of some of these experiments on aluminum rod exposed to the weather for 10 months are given in Table II. These data, as well as those of other similar tests, show significantly that water vapor is liberated by the oxide coating at all temperatures from 70° F. up to or close to the melting point of aluminum. More important, however, is the fact that the major portion of the water which is liberated as such comes off at temperatures below about 300° C. (575° F.). At higher temperatures the proportion of hydrogen to water vapor is greatly increased. This indicates that part of the water is more firmly held (combined as the trihydrate) and there is a greater tendency for the water vapor to react with the metal to form

Table I—Crystal Structure and Density of the Various Forms of Alumina and Alumina Hydrates

ALUMINA FORM	FORMULA	MINERAL NAME	CRYSTAL STRUCTURE	LATTICE CONSTANT			REFRACTIVE INDICES	DENSITY
				A	B	C		
Alpha-alumina*	$\alpha\text{Al}_2\text{O}_3$	Corundum	Hexagonal	5.12	—	6.98	$\epsilon = 1.760$ $\omega = 1.768$	4.0
Gamma-alumina	$\gamma\text{Al}_2\text{O}_3$	—	Cubic	7.9	—	—	$\eta = 1.696$	3.4
Alpha-monohydrate	$\alpha\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Böhmite	Orthorhombic	3.78	11.8	2.85	$\alpha = \beta = \gamma = 1.624$	3.0
Beta-monohydrate	$\beta\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Diaspore	Orthorhombic	4.43	9.36	2.82	$\alpha = 1.702$ $\beta = 1.722$	3.4
Alpha-trihydrate	$\alpha\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Gibbsite	Monoclinic	8.62	5.06	9.69	$\gamma = 1.750$	2.42
Beta-trihydrate	$\beta\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	"Bayerite"	—	—	—	—	$\alpha = 1.566$ $\beta = 1.566$	2.5
							$\gamma = 1.857$	

*Melting point about 2030° C. (3685° F.).

hydrogen at the higher temperatures. In the particular series of tests summarized in Table II, heating was not carried beyond 600° C. (1110° F.) but in a similar series of tests a further evolution of gas was noted on heating the metal to the melting point.

Protection by Oxide Films

From the viewpoint of oxidation and corrosion, the reactions of metallic aluminum with oxygen and water are of the greatest importance. Under many conditions, these reactions are self-stopping because an impervious oxide film is present or forms on the aluminum; thus, many reactions with metallic aluminum proceed only to a limited degree. At elevated temperatures, or in the presence of reagents which attack the oxide film, the reactions will proceed further and more rapidly.

With oxidizing reagents or under oxidizing conditions, the film tends to remain intact and the reaction rate is low. The principal reason why the oxide film offers such effective protection is that it is relatively insoluble in the corrosive media generally encountered. In fact, aluminum and its oxide are relatively stable in weakly acid solutions. One liter of water will dissolve only about 1 mg. of Al_2O_3 (0.5 mg. of aluminum) at a temperature of 18° C. In strong acid solutions, and more particularly in alkaline solutions, the oxide film and the metal are attacked more readily.

Table II — Water and Gas Liberated From Aluminum Rod¹

(P. T. Stroup, Aluminum Research Laboratories)

TEST	PREHEATING ² IN DRY AIR	GAS EVOLVED ON HEATING IN VACUUM TO 600° C. ³	
		WATER VAPOR	GAS ⁴
No. 1	None	69	68
2	2 hr. at 165° C.	24	41
3	2 hr. at 260° C.	20	33
4	3 hr. at 360° C.	3.5	15
5	4 hr. at 455° C.	1.9	9.8
6	3 hr. at 465° C.	1.0	10.6
7	12 min. at 500° C.	1.5	7.0
8	26 min. at 500° C.	Tr ⁵	3.8

¹Extruded 2-in. rod (99.3% Al), exposed outdoors 10 months before testing. Samples were short lengths with surface area of about 196 sq.cm.

²Period of preheating in current of dry air before heating *in vacuo* to collect gas.

³Gas evolved on subsequent heating *in vacuo* to about 600° C. (1110° F). Units represent milliliters under standard pressure and temperature (760 mm., 0° C.) per 1000 sq.cm. of aluminum surface.

⁴Hydrogen, carbon dioxide, carbon monoxide and traces of sulphur-containing gases.

⁵Some, but not enough to measure.

McKee and Brown¹⁰ state that the resistance of aluminum to corrosion is influenced to an appreciable extent by the particular form of oxide film that is present on an aluminum surface and by the solubility of the corrosion products that are formed. In their experiments, aluminum sheet (Alloy 2S-H14) showed a weight loss of only about 0.02 mg. per sq.cm. per day when immersed in dilute solutions of mineral acids having a pH of 4.5 or higher. They show that the rate of attack, however, is influenced by the specific anion or cation present in the corrosive mediums. In general, the oxide film on aluminum sheet is resistant to attack in weakly acid solutions, but is significantly attacked in solutions of sodium hydroxide or sodium carbonates having a pH above about 8.5.

It is a well-known fact that very high-purity aluminum (99.95% Al) is more resistant in many corrosive environments than commercially pure aluminum (99.0% Al) or any of the various aluminum alloys. This is attributed to the fact that on the very high-purity material the oxide film is much more continuous and does not contain other oxidation products from the various alloying elements that are present in solid solution or as inter-metallic compounds.

To illustrate the difference in continuity and structure, micrographs of thin sections of oxide coatings formed by electrolytic oxidation in a sulphuric acid electrolyte are shown in Fig. 5 and 6, reproduced from a paper by the present authors entitled "The Structure of Anodic Oxide Coatings" in *Transactions A.I.M.E.*, Institute of Metals Division, V. 156, 1944, p. 288. The oxide coating illustrated by Fig. 5 was formed on a sample of high-purity aluminum sheet (99.95% Al) and is continuous and very transparent. It consists principally of Al_2O_3 , as the metal contained only very small amounts of alloying elements (less than 0.05%). For comparison, an oxide coating formed on 2S-O sheet (99.2% Al, balance Fe, Si and Cu) is shown by Fig. 6. Owing to the numerous particles of α (Al-Fe-Si) and (Al-Fe) constituents that are normally present in this alloy, the coating is less continuous and protective, as it contains oxidation products of the elements in solid solution as well as oxides from the various intermetallic compounds that are present as microconstituents.

The features that are shown in these micrographs apply to the natural oxide films that form on aluminum and its alloys, and in part explain why different alloys vary in their resistance to weathering.

¹⁰"Resistance of Aluminum to Corrosion in Solutions Containing Various Anions and Cations", by A. B. McKee and R. H. Brown. *Corrosion*, V. 3, Dec. 1947, p. 5.

The protectiveness of the oxide film on commercial alloys is modified by the electrochemical characteristics of the constituents and occluded substances that interrupt the continuity of the natural oxide or artificial films. Some of these constituents may be anodic to the aluminum; others may be cathodic. When such conditions prevail, local cells are formed which lead to local galvanic action in the presence of an electrolyte. When such potentials exist, anodic solution may occur and the metal will dissolve beneath the oxide film; the film may flake off or be pushed off by corrosion products that form beneath it.

The films that form on aluminum alloys during annealing and heat treatment are more protective for several reasons: In the first place, they are considerably thicker than the film formed at normal temperatures. Secondly, the films formed at elevated temperatures are inherently more resistant to corrosion or chemical attack — films produced during heat treatment, as well as anodic oxide films, are much more difficult to strip than those which have not been heated.

An interesting example of the relative insolubility of an aluminum oxide film produced by thermal treatment was obtained by R. H. Brown in the course of some experiments in Aluminum Research Laboratories to determine the resistance of high-purity aluminum (99.95%) to strong hydrochloric acid solutions. In making the specimens for these experiments, he heat treated some of the high-purity aluminum sheet samples for 30 min. at 625° C. (1150° F.), and then slowly cooled them to room temperature. The specimens were then subjected to corrosion in a 25% hydrochloric acid solution. The condition of a specimen after two days is shown by Fig. 7. The interesting features of this photograph are the flakes of oxide film that separated from the specimen. Apparently this film was relatively stable even in the 25% hydrochloric acid solution and, because of its insolubility, Brown found it expedient to remove the heavy film formed during heat treatment by machining in order to observe the effects of the hydrochloric acid solution on the high-purity aluminum.

Removal of Oxide From Aluminum

Frequently it is necessary or desirable to remove the existing natural oxide film on various products and replace it with a film that is thinner, more uniform, or that has other specific properties. This is particularly true, for example, in the cleaning of aluminum alloys for spot welding, where a surface with low and uniform resistance is required. It is also important in the preparation of test specimens for the determination of the

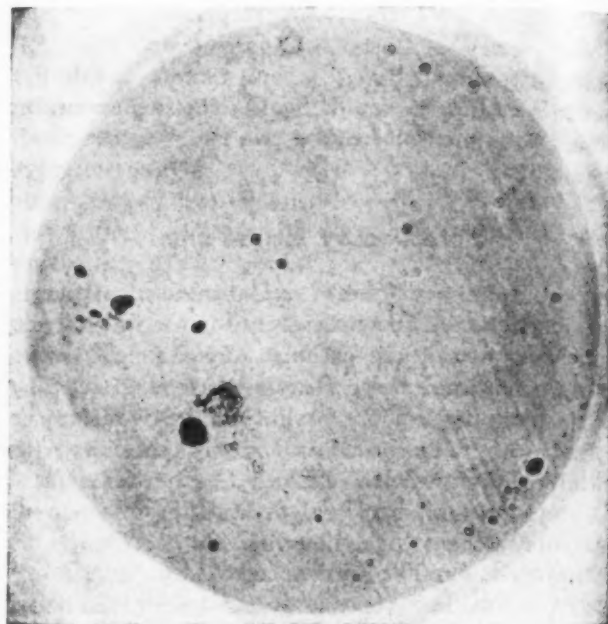


Fig. 5 — Thin Section of Oxide Film From Anodically Coated Sample of High-Purity Aluminum Sheet (99.95% Al). 500X. Note the transparency of the film (by transmitted light) and relative absence of occluded constituents

relative resistance to corrosion of various types of aluminum products. (From what has been said in the first part of this paper, it is obvious that it is impossible to prepare and maintain an aluminum surface free from an oxide film in any atmosphere containing oxygen or water.)

An old oxide film can be removed mechanically by machining or by abrasion, but a new film instantly starts to form. If this new film is to be kept to a minimum thickness, as little heat as possible should be developed during the operation. No lubricant should be employed, as it will be adsorbed by the newly formed oxide film and resist solvents. Even the solvent may be adsorbed!

There are acid and alkaline solutions which are effective in removing oxide, but after rinsing and drying the parts will still have an oxide film which re-formed during the treatment. The new film, however, may have more desirable properties for some specific application. The case just mentioned of securing low and uniform electrical resistance is an interesting example. Hess, Wyant and Averbach¹¹ have investigated a variety of

¹¹"The Surface Treatment of Alclad 24S-T Prior to Spot Welding", and "The Surface Treatment at Room Temperature of Aluminum Alloys for Spot Welding", by W. F. Hess, R. A. Wyant and B. L. Averbach, *Journal of the American Welding Society*, Research Supplement, V. 9, 1944, p. 402 and 417, respectively.

cleaning procedures and have tested the resulting surfaces by measuring the resistance between two pieces when held together under a high standard pressure. Results with Alclad 24S-T4 sheet showed that an initial test-resistance of 1000 microhms or over could be reduced to 10 microhms or less by the best of the acid treatments investigated.

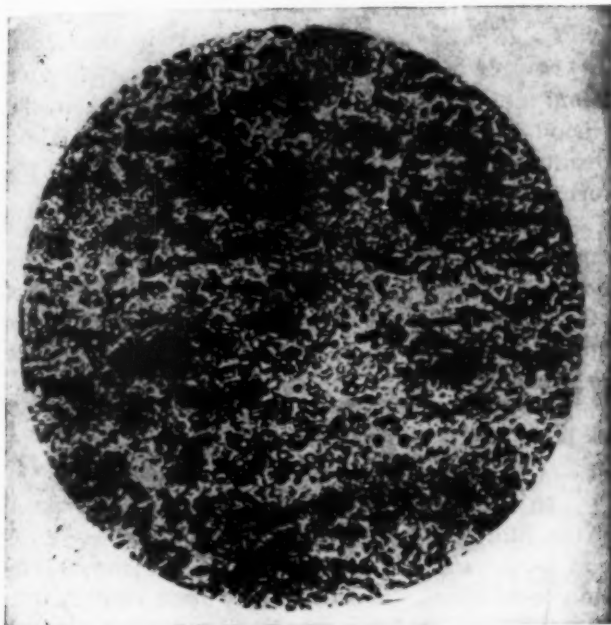


Fig. 9 — Thin Section of Oxide Film From Anodically Coated Sample of Commercial Aluminum Sheet (99.2% Al). Photographed at 500 \times by transmitted light. The oxide film is translucent from the occluded oxidation products of alloying elements and constituent particles

The characteristics of the oxide coating on the sheet have an important effect on the time required to remove it. The oxide film on sheet heat treated in air appeared to dissolve more readily than that on sheet heated in molten nitrate. Generally speaking, when the oxide film was removed by an aqueous reagent, the resistance of the film which eventually re-formed was substantially higher than when the film was removed mechanically by wire brushing. The resistance of the new film, moreover, was affected in an important way by the solution employed — which would indicate that some of the reagents employed were adsorbed in the new film, incompletely removed by washing, and thereafter influenced the rate of film formation.

Some recent work by Durkin¹² on the removal of surface oxide from aluminum also shows that

¹²"Surface Oxide Removal Important in Final Processing of Aluminum", by D. E. Durkin. *Materials and Methods*, V. 27, No. 4, 1948, p. 82.

the type of solution and the time of treatment have an important bearing on obtaining a low and uniform surface resistance, and on the extent and rate of formation of a new film which would tend to increase the surface resistance.

Mechanism of Film Formation

The unique characteristics of natural oxide films on aluminum have led to much speculation as to the mechanism of their growth. The detailed



Fig. 7 — Large Flakes of Oxide Film Peeling From High-Purity (99.95% Al) Aluminum Sheet After Two Days in a 25% Hydrochloric Acid Solution. The film, formed during heating at 625°C., appears to be relatively insoluble. (R. H. Brown)

treatment of this aspect of film formation, however, is beyond the scope of this paper and will be mentioned only briefly.

From the available evidence, it would appear that the films which form on pure aluminum in dry oxygen or dry air are of a type we have called the "barrier layer"—an impermeable film which has grown to a thickness just sufficient to prevent the transfer of ions necessary to sustain further growth. The thickness is a function of the temperature (and perhaps of other factors). Water or water vapor plays an important part in the continued growth of oxide films on aluminum; under favorable conditions the film may continue to grow to a thickness substantially greater than that of the barrier layer.

This would be explained on the basis of changes taking place in the outer layer of the film which, in effect, increase its porosity or permeability to oxygen or water vapor. These changes might result from adsorption of water vapor and hydration of the film. At the base of this thick oxide film, however, there would always be a barrier layer of equilibrium thickness.

The formation of a natural barrier layer of oxide is considered analogous to that of the dielectric film on aluminum for electrolytic condensers. Such dielectric films are formed by electrolytic oxidation in certain electrolytes in which the oxide that forms is virtually insoluble. These films grow quickly to an equilibrium thickness for each formation voltage, effectively blocking further passage of appreciable current; no significant increase in thickness can be obtained unless the voltage is increased. Thus, it seems that the thickness of a film of this type is limited by the ability of ions and electrons to pass through the barrier layer film, and as its thickness increases, more energy is required for the transfer.

T. P. Hoar and L. E. Price as well as N. F. Mott¹³ have theorized on the mechanism of film formation. Mott believes the formation of a thin protective oxide film on aluminum can be explained on the basis of two assumptions: (a) that positive metal ions can leave the metal and diffuse through the oxide to combine with oxygen at the oxide-air interface to form new oxide, provided electrons can also pass from the metal to the free surface; (b) that electrons can get through the oxide layer either by thermionic emission into the conduction levels of the oxide, or by the quantum-mechanical

tunnel effect. More recently he has proposed another hypothesis in which he assumes that if oxygen is adsorbed on the surface of the oxide and oxygen ions are formed, a strong electrical field will be set up in the oxide, saying that migration of ions can take place under the effect of these fields. Mott is not certain which of the mechanisms he proposed for limiting film growth is valid, and states that possibly both may be operative in certain temperature ranges.

Cabrera, Terrien and Hamon,¹⁴ in describing the results of their research on the oxidation of aluminum in a dry atmosphere, comment on the various mechanisms suggested by Mott. Their results indicate that the thin oxide films are formed by the diffusion of Al^{+++} ions.

The exact mechanism by which the barrier-layer oxide film is formed, as well as many phenomena observed in the formation of oxide films on aluminum, will undoubtedly continue to offer an interesting field of research for a long time to come.

Summary

In summary, it may be said that the natural oxide film on aluminum is amorphous, as far as can be determined by X-ray and electron diffraction techniques. However, at a high enough temperature it can be converted to gamma-alumina and, on exposure to weather, some hydration occasionally occurs.

As to normal behavior, the natural and weathered films are adsorptive, particularly with respect to water vapor. Upon heating, water vapor, hydrogen, and small amounts of carbon dioxide are liberated. Most of the water vapor is liberated as such below 300° C. (575° F.), and at higher temperatures larger proportions of hydrogen and other gases come off.

The protective action of the film depends to a large extent upon its continuity and its rate of dissolution in the media to which it is exposed. Continuity of the film is fundamentally affected by the alloying constituents in the basis metal, and by the oxidation products thereof which may exist in the film. Rate of dissolution of the film is influenced by thermal treatments the oxide may previously have received.

An old film can be removed by mechanical means or by solution with chemical reagents. The properties of the new film, which forms at once, are influenced by the method used for removing the old film of oxide.

¹³"The Electrochemical Interpretation of Wagner's Theory of Tarnishing Reactions", by T. P. Hoar and L. E. Price; *Transactions of the Faraday Society*, V. 34, 1938, p. 867. "Theory of the Formation of Protective Oxide Films on Metals—II", by N. F. Mott; *Transactions of the Faraday Society*, V. 36, 1940, p. 472.

¹⁴"On the Oxidation of Aluminum in a Dry Atmosphere", by N. Cabrera, J. Terrien and J. Hamon. *Comptes rendus*, V. 224, 1947, p. 1558.

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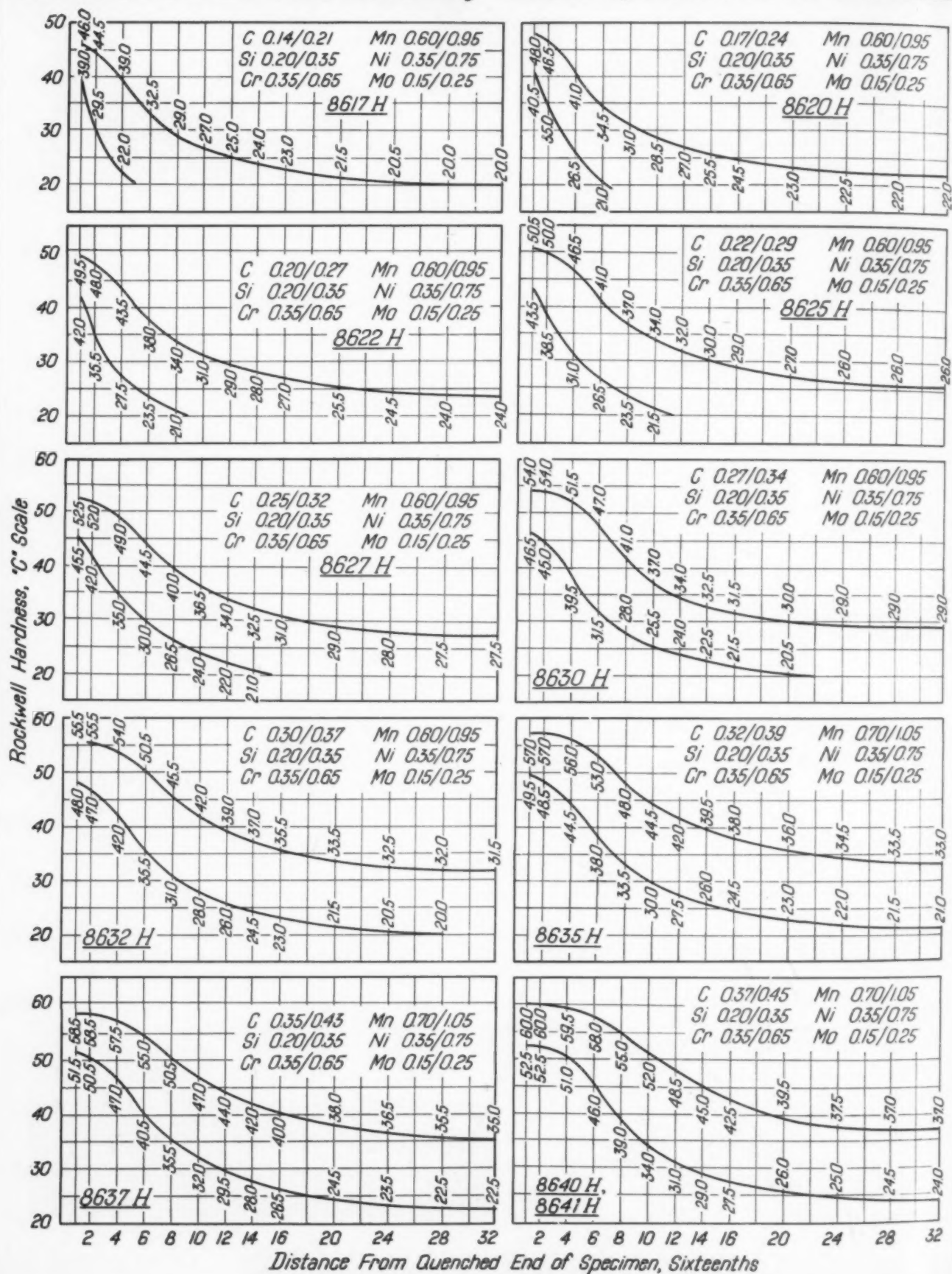
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"Current Theories of the Hardening of Steel"—50 Years Later

By J. B. Austin

Director of Research
U. S. Steel Corp.
Kearny, N. J.

For the subject of the 1948 Sauveur Memorial Lecture of the Boston Chapter, A.S.M., J. B. Austin revived a title twice used by Professor Sauveur. The article presented here is based on the lecture, and brings up to date the ever-current topic of the theory of the hardening of steel. Aside from the importance of Dr. Austin's paper as a contribution to current metallurgical literature, publication in Metal Progress is timely since it may remind readers of the forthcoming dedication of the Sauveur Memorial Room in A.S.M. headquarters in Cleveland on Aug. 19.

IN 1896 Albert Sauveur presented before the American Institute of Mining Engineers a stimulating paper entitled "The Microstructure of Steel and the Current Theories of Hardening",¹ which was recognized as a pioneer contribution to metallography and which touched off a debate on theories of hardening steel that continues even today. It brought out discussion from such men as Ledebur, Hadfield, Arnold, Roberts-Austen, Campbell, Osmond, and Howe, whose comments, together with Sauveur's reply, filled 100 printed pages in the *Transactions* of the Institute.

The first section of this paper described many interesting details of the metallographic art as it was then practiced. Among other topics were the advantages of concentrated nitric acid and of

tincture of iodine as etching agents, and the utility of polishing in relief without the use of etching agents. The reader is also warned that: "A magnification of at least 300 diameters is required to resolve the structure of pearlyte." This appears to have been close to the limit of the equipment then available, which explains much of the difficulty that the early metallographers experienced in identifying microstructures.

The second part dealt with current theories of hardening steel and attempted to decide between the two chief views then popular, each of which, in the subsequent discussion, was defended violently by its adherents. Both theories agreed that quenching preserved to room temperature a special structure that was assumed to be stable at red heat but unstable at a lower temperature. They

differed, however, in the nature of this special structure, or condition.

The carbon theory held that on heating steel above a critical temperature, which sometimes seems to have been taken as that of the magnetic inversion, carbon passed from its normal condition as "cement carbon" to a special form called "hardening carbon", which was unstable below that temperature, tending to pass back to "cement carbon" on slow cooling. When preserved by sudden cooling, however, it resulted in hardened steel.

The contrary view held that the action of carbon was only indirect, that above the critical range iron passed spontaneously into a strong, hard, brittle, allotropic state called beta iron, which was unstable at lower temperature, but which transformed slowly so that it could be preserved by quenching.

Although Sauveur was accused of favoring the

¹*Transactions* of the American Institute of Mining Engineers, V. 26, 1896, p. 863. Discussion in V. 27, 1897, p. 846.

allotropic theory, he seems to have attempted to be impartial, an attitude that led him to define martensite as "the constituent of steel which exists at a high temperature, and being retained by sudden cooling confers hardness upon quenched steel".

An Appraisal (in Retrospect)

When read today these discussions seem archaic and at times naive. They remind us of the blind men examining the elephant; each based his opinion on observations over a very limited range and each arrived at a conclusion containing elements of truth but short of the whole truth, which was eventually revealed by combining the several diverging views.

Yet one should not yield to the easy temptation of ridiculing this apparent naiveté. In the first place, I venture to suggest that we today are in many respects as unsophisticated as were these early pioneers and that 50 years from now many of our current debates will appear no less artless. In the second place, to do so would grossly undervalue the contributions made by these early investigators. I sometimes fear that many of us fail to realize how close they came to many of our modern views, which they failed to achieve only because they lacked proper instruments or because their views were too advanced to gain recognition.

Two examples will serve to illustrate this point. The first is described by Professor Sauveur in his delightful pamphlet "Metallurgical Reminiscences".

In 1896 my microscopical work was temporarily interrupted because of the discovery of X-rays by Roentgen in the latter part of 1895. In January 1896 — that is, a very few months later — at the suggestion of W. R. Walker, experiments were undertaken to ascertain whether by the use of such rays internal defects in steel could not be detected. My outfit consisted of a "Crookes" tube, an induction coil and a storage battery. Obviously, with such crude appliances, the rays we were able to generate failed to penetrate even the thinnest steel sheets. Our experiments, however, attracted enough public attention to warrant first-page reports in the newspapers of the day and for a while we enjoyed intense publicity. I believe it can be claimed that we were probably the very first to enter the field of radiography.

Failing to obtain results with steel, I turned my attention to a substance less resistant to penetration, namely, the hand of my assistant, W. C. Post, and obtained a very satisfactory picture. I have a vivid recollection of the thrill I experienced when the bone structure of Post's hand flashed into view in the developing tray.

The second example, which has been called to my attention by J. R. Vilella, also concerns Pro-

fessor Sauveur. In the first edition of "The Metallography of Iron and Steel", in the discussion of the thermal critical points of steel, there appears the following paragraph:

LeChatelier rightly reminds us that the speed of the transformations occurring at the critical points of steel follows the general laws which govern the speed of all chemical phenomena. In other words, that the speed of the transformation is the greater (1) the higher the absolute temperature and (2) the wider the range between the actual temperature and the temperature of equilibrium, that is, the temperature at which the transformation is due. Above the critical temperature both influences act in the same direction and the speed of transformation increases without limit. Below the critical temperature these influences act in opposite directions necessarily giving rise to the existence of a maximum speed. According to LeChatelier this notion of variable speeds of transformation accounts for all the peculiarities of the hardening treatment. *On heating it is hardly possible to raise the temperature of transformation more than 100° C. through very rapid heating, while during cooling the speed reaches its maximum at about 600° C., is very feeble below 200, and nearly null at atmospheric temperature.*

I should like to direct your attention particularly to the last sentence (the italics are mine) because it describes succinctly the most significant feature of isothermal transformation processes in steel. This statement must have attracted but little attention, for it was deleted from later editions of this work; yet it serves to demonstrate the lines along which metallurgical leaders were thinking at the beginning of the century and to show how close they came to our modern concepts.

This last example leads me to wonder whether today metallurgists are not paying overmuch attention to gadgetry, to the neglect of developing the vision and the precision of thought which characterized these early investigators.

Sauveur's Questionnaire of 1926

In 1926 Professor Sauveur decided to review the subject of theories of hardening and he circulated among a group of 29 illustrious metallurgists a questionnaire containing the following:

1. What in your opinion is the nature of martensite and what causes its hardness?
2. What are the conditions necessary for its formation and the mechanism of that formation?
3. If you believe it to be a solid solution of iron and carbon or of iron and the carbide Fe_3C , what position do you think the carbon atoms or the carbide molecules occupy in the space lattice of the crystals?
4. What part, if any, do you think that strains play in the hardening of steel?

The replies to these questions were summarized by Sauveur and were presented in a paper

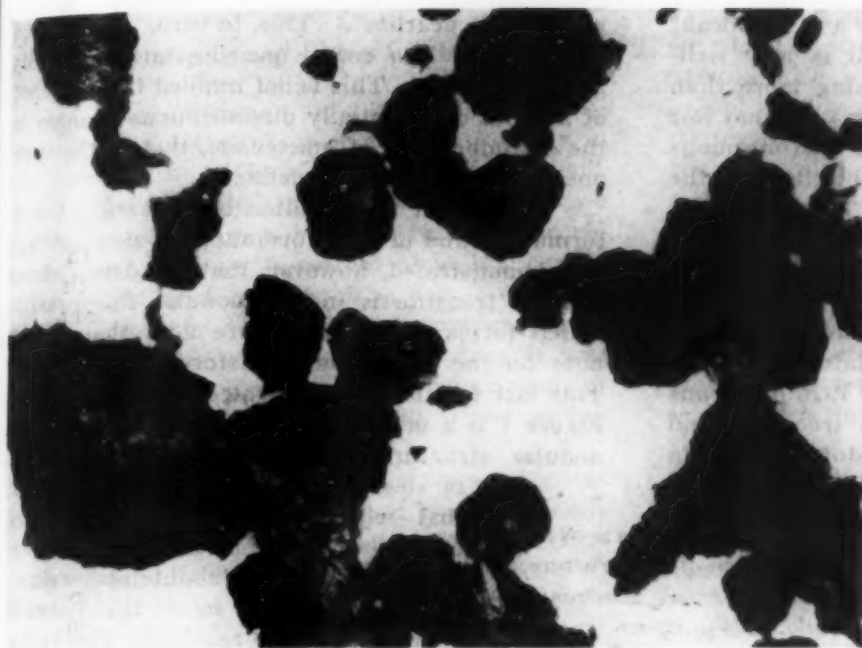


Fig. 1 — Nodular Fine Pearlite, Also Called Nodular Troostite, in Eutectoid Carbon Steel. 750X. (Vilella)

before the A.I.M.E. entitled "Current Theories of the Hardening of Steel Thirty Years Later".² The results indicated, as one might have expected, about as wide divergence of opinion as in 1896.

They are described by Sauveur: "Comparing the situation today with that of thirty years ago as presented in my first paper, the only progress (?) made toward a solution of the problem may, I believe, be thus summarized: (1) abandonment of the belief in the existence of beta iron; (2) X-ray analysis of iron-carbon alloys, by which it is shown that gamma iron has a face-centered space lattice, and alpha iron, as well as the iron present in martensite, a body-centered space lattice; and (3) the belief expressed by some that the hardness of martensite might be caused primarily (a) by the presence of extremely small (submicroscopic) ferrite grains, or (b) by the distortion of the space lattices resulting from the presence of carbon atoms in enforced solid solution. This does not constitute a very material advance, if advance at all, seeing that it has also introduced additional controversial matter."

Having summarized the views of others, Professor Sauveur then stated his own, which differed in many respects. They were in part:

Austenite is a solid solution of carbon, probably in the form of the carbide Fe_3C , in gamma iron.

Troostite is a solid solution of carbon, probably in the form of the carbide Fe_3C , in beta iron.

²Transactions of the American Institute of Mining and Metallurgical Engineers, V. 73, 1926, p. 859.

Austenite always transforms into troostite regardless of the temperature at which the transformation takes place.

Martensite is an aggregate of austenite and troostite, necessarily resulting from the gradual transformation of austenite into troostite.

The hardness of martensite increases with its carbon content because of the greater hardness of the troostite it contains, and possibly also because finer needles and finer grains result from the transformation of austenite containing much carbon.

These quotations make it clear that Sauveur did not concur in many of the answers sent to him.

Beta Iron, Troostite, Sorbite

As 22 years have elapsed since this paper was written, and 52 years have passed since the publication of the first paper, it seems fitting to review the subject once more, in the light of present knowledge, to see how many of these controversies have been settled, how many remain, and what new questions have been raised.

One question which has been settled beyond

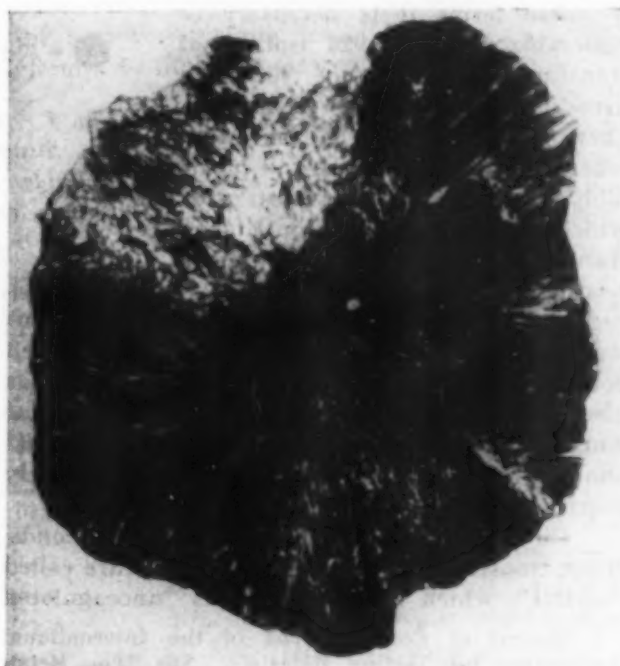


Fig. 2 — A Nodule of the Pearlite in the Field of Fig. 1, Magnified to 2000X. (Vilella)

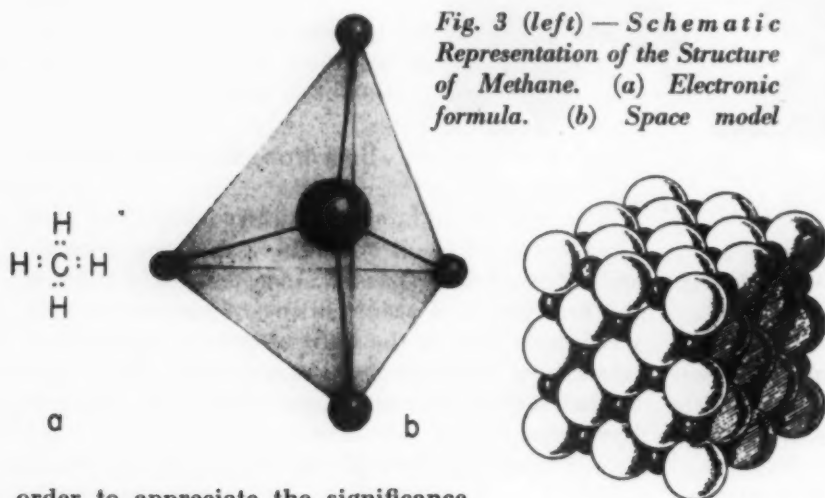
doubt is that beta iron does not play any significant role in the hardening of steel. It is now well-established that beta iron is nothing more than alpha iron (body-centered cubic iron) that has lost its ferromagnetism. There is no discontinuous change in crystal structure in passing through the Curie temperature; consequently, there is no discontinuous change in the solubility of carbon. Insofar as theories of hardening steel are concerned, one can therefore forget beta iron.

Another matter that has been greatly clarified in the last 20 years is the nomenclature of microconstituents in steel. In Sauveur's 1926 paper one frequently encounters the terms "troostite" and "sorbite", which are used but seldom today. In

irresolvable pearlite".³ This, in turn, was believed to coagulate into coarse pearlite and eventually into spheroidite. This belief implied the existence of a series of essentially discontinuous changes in the decomposition of martensite, though the various steps were not well-defined.

Subsequent investigation of isothermal transformation, and of transformation on slow cooling, has demonstrated, however, that the dark-etching nodular troostite is in fact nodular fine pearlite which forms at a temperature near that of the nose on the isothermal transformation diagram. This last fact is well illustrated by Fig. 1 and 2. Figure 1 is a micrograph at 750 diameters of the nodular structure (formerly called troostite)

in steel cooled at a rate just short of that required to make the structure completely martensitic. Figure 2 is a micrograph of a nodule at a magnification of 2500; in it the lamellar pearlite is clearly resolved. This nodu-



order to appreciate the significance of these terms it is necessary to remember that in 1926 isothermal transformation had not yet been investigated and many metallographers believed with Sauveur that when austenite decomposed, it invariably transformed first to martensite, which, being unstable, could then transform to other structures during heating. The first of these, called "troostite", was regarded not as a definite structure in itself but was defined rather loosely as "an uncoagulated conglomerate of transition stages".³ The term was also used to designate the dark-etching nodular constituent obtained by cooling steel at a rate just short of that required to make the steel completely martensitic.

On further heating under appropriate conditions, troostite transformed into a structure called "sorbite", which was described as "uncoagulated

³Report of Committee 53 of the International Association for Testing Materials. See "The Metallography of Iron and Steel", by A. Sauveur. 2nd edition, 1920, p. 460.

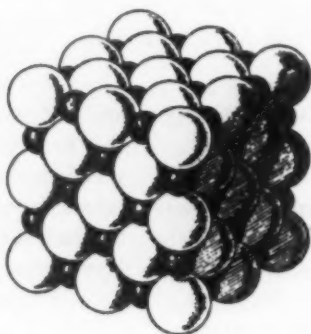
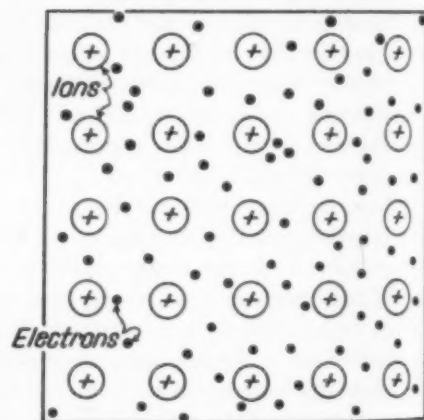


Fig. 4 — Representation of the Structure of Sodium Chloride. Ionic bonding of sodium and chlorine ions

Fig. 5 (below) — Schematic Representation of the Structure of a Metal: Positive Metallic Ions Surrounded by an Electron "Gas"



lar product is still sometimes called primary troostite, though the term has not gained widespread acceptance. Moreover, in order to avoid confusion and the implication of a series of discrete steps in the decomposition of martensite, the structures formerly called troostite and sorbite are now generally designated "tempered martensite". However, the idea of steps in the tempering of martensite has been retained in another connection, which will be discussed later.

Since the first step in the hardening of steel is the formation of austenite, it is helpful to know something of the nature and structure of this phase. Sauveur clearly recognized this, though he did not incorporate it specifically in his questions.

Austenite and Other Crystals

As noted, Sauveur in 1926 described austenite as "a solid solution of carbon, probably in the form of the carbide Fe_3C , in gamma iron". The word "probably" in this statement was an expression of the prevailing uncertainty concerning whether carbon was present as atomic carbon or as molecules of carbide. The debate over this question provoked considerable discussion, particularly along thermodynamic lines, since it was hoped at that time that a thermodynamic point of view might yield a definitive answer. However, the data available proved inadequate.

The answer eventually came from advances in our knowledge of the nature of chemical bonds and since this knowledge has many applications in metallurgy, I should like to discuss it briefly in simplified, perhaps oversimplified, terms.

The traditional concept of a molecule was that of a relatively small number of atoms closely bound by chemical forces to form a chemical unit of definite composition and properties. A typical example was the molecule of methane, the structure of which is shown schematically in Fig. 3, in which four hydrogen atoms are bound to a central carbon atom by strong bonds that are now known to result from the sharing of electrons between carbon and each of the four atoms of hydrogen. Such bonds can be thought of as direct linkages between the atoms, as indicated by the electronic formula presented at the left of Fig. 3.

Under ordinary conditions, methane is a gas in which individual molecules are free to move around with little interaction among themselves except on direct collision. As the temperature is decreased, however, cohesive forces among the molecules increase until at about -160°C . (-255°F .) methane liquefies. At about -185°C . (-300°F .) it freezes, yielding a solid composed of molecules held together by cohesive forces but still identifiable as individual units. This type of solid is characteristic of most organic compounds.

Among inorganic compounds, however, the state of affairs is quite different because the chemical bond is in general not a linkage formed by the sharing of electrons between specific atoms but results from the transfer of an electron from one atom to another, thus yielding charged atoms, which are held together by electrostatic attraction. For example, in sodium chloride the sodium atoms each lose an electron to form a positive sodium ion, whereas each chlorine atom gains an electron to form a negative chlorine ion. The structure of solid sodium chloride is therefore that shown in Fig. 4, in which each type of ion is surrounded by a cluster of ions of opposite sign. In this arrangement there is no definite unit that retains the identity of a molecule, unless the entire crystal is regarded as one giant molecule.

In a solid metal the structure is again different. The metal atoms may be thought of as losing their valence electrons, leaving a positively charged metal ion; but the electrons thus freed are not taken up by other atoms. Instead they remain as a kind of electron gas, which permeates the lattice of metallic ions. Figure 5 is a crude attempt to illustrate this concept.

When a metal is alloyed by the addition of another metallic element, the atoms of the solute commonly take one of the lattice sites occupied by solvent atoms to form a substitutional solid solution. When atoms of a nonmetallic element are added, however, they tend, if they can fit, to go to interstices in the lattice of solvent atoms to form an interstitial solid solution.

More specifically, when carbon is introduced into gamma iron, it occupies the spaces between the iron atoms. Moreover, carbon atoms cannot form direct linkages of the methane type with iron atoms, and it is difficult to see how they can build up an ionic structure such as occurs in sodium chloride. The most likely type of bond is something resembling a

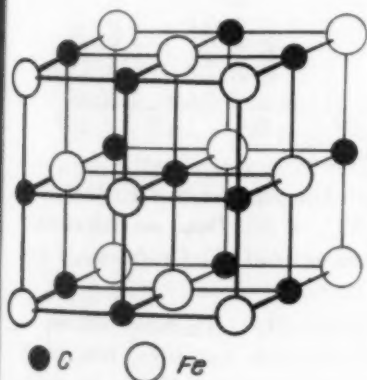


Fig. 6 (above) — The Structure or Atomic Arrangement of Austenite, According to Petch

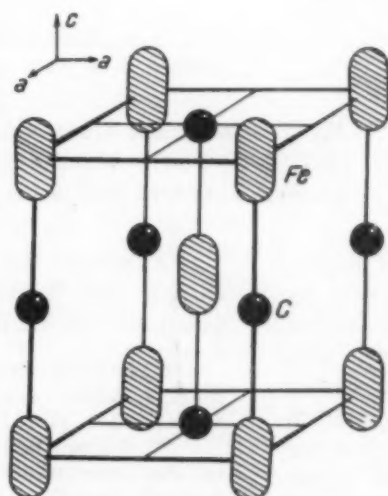


Fig. 7 — The Probable Structure of Martensite, According to Lipson and Parker

metallic bond, which means that carbon atoms are not directly linked to specific iron atoms to form a molecule in the traditional sense. When carbon migrates through gamma iron, it simply moves from one site to another without any corresponding movement of iron atoms bonded to it. It is therefore no longer permissible to think of iron carbide molecules of the traditional type existing in solution in iron.

The positions occupied by the carbon atoms in austenite have been determined by Petch⁴ by means of X-rays, with results shown in Fig. 6. Carbon atoms occupy positions at the center of the unit cell and at the midpoints of the edges. Although the figure shows all the sites that carbon can occupy, there are, in fact, never enough carbon atoms present to fill all the possible positions. Indeed, in austenite containing 1.7% C, which is about the maximum, only one position out of twelve is occupied.

The nature and structure of the austenite from which martensite forms can therefore be regarded as well-established. It is an interstitial solid solution of carbon in gamma iron, with the atoms arranged as shown in Fig. 6.

Martensite

The arguments advanced above likewise answer Sauveur's question concerning whether carbon in martensite exists as atoms of carbon or molecules of iron carbide, since there is again no basis on which to speak of carbide molecules existing within the iron lattice.

But what then is the precise structure of martensite? What is the structure of iron in which the carbon atoms are dispersed and what positions in the structure do the carbon atoms occupy? As with austenite, X-ray diffraction data yield a partial answer, though it is by no means so complete or so certain.

In 1926, the year of Sauveur's second paper, Fink and Campbell⁵ showed that martensite is tetragonal, a finding that, within the next five years, was verified by other investigators, who showed also that the lattice parameters varied linearly with carbon content. On extrapolation to zero carbon content they obtained a parameter which agreed with that of body-centered cubic iron. On this basis, martensite can be considered as ferrite supersaturated with carbon.

The next step, the assignment of locations to the atoms in the unit cell, as has already been

discussed for austenite, is more difficult. It has been attempted by a number of investigators, the most recent, and perhaps most successful, work being that of Lipson and Parker.⁶ They conclude that the martensite structure is that shown in Fig. 7, in which there is the customary body-centered tetragonal unit cell with the carbon atoms occupying the largest interstitial holes. The iron atoms, however, seem to be displaced from the exact corners and center of the cell, sometimes by as much as 10%. One interpretation, which is, however, not beyond question, is that the interstitial holes are not large enough to accommodate carbon atoms comfortably, so that the surrounding iron atoms are displaced, mainly in the vertical direction, as shown.

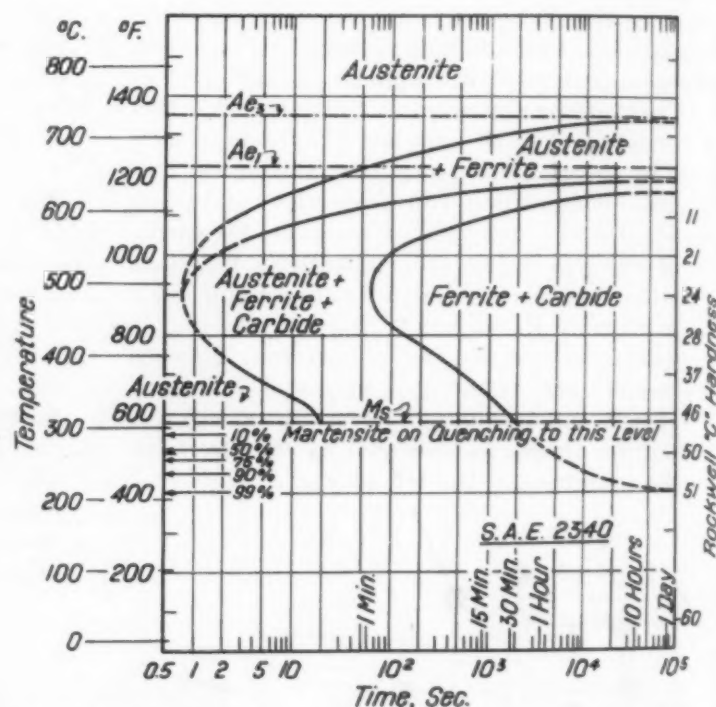


Fig. 8—Isothermal Transformation Diagram for S.A.E. 2340 Steel (0.37% C, 0.68% Mn, 3.41% Ni), With Data on Martensite Formation Added. Steel austenitized at 1450° F. Grain size, 7 to 8

Although this schematic structure shows a carbon atom in each possible location, few such positions are in fact occupied. Indeed, as with

⁴"The Positions of the Carbon Atoms in Austenite", by N. J. Petch. *Journal of the Iron and Steel Institute*, V. 144, 1942, p. 111.

⁵"Influence of Heat Treatment and Carbon Content on the Structure of Pure Iron-Carbon Alloys", by W. L. Fink and E. deM. Campbell. *Transactions of the American Society for Steel Treating*, V. 9, 1926, p. 717.

⁶"The Structure of Martensite", by H. Lipson and Audrey M. B. Parker. *Journal of the Iron and Steel Institute*, V. 149, 1944, p. 123.

austenite, not more than 1/12 of these locations are occupied even at 1.7% carbon. Moreover, the actual displacement of the iron atoms at any given location in the structure seems to depend on the number of adjacent atoms of carbon.

This is the best answer that can now be given to Sauveur's first question as to the nature of martensite. It is admittedly not established beyond question, nor is it satisfactory in all details. More investigation is needed but this does not alter the fact that we are fairly well along toward a definite answer. Certainly, marked progress has been made.

The second half of Sauveur's first question deals with the cause of the hardness of martensite and here I must confess there has been but little progress in the last 22 years. This is in part because there is no exact definition of hardness. The hardness of martensite is probably associated with its tetragonal structure, which is essentially a structure distorted by the presence of carbon atoms and possessing no planes on which gliding

point, which is determined by the composition of the metal. Moreover, for each increment of temperature below the M_s point, an increment of martensite forms almost instantaneously. The speed of formation of a single martensite blade in steel containing 1.7% C was found by Wiester⁷ to be of the order of 0.001 sec. If the cooling is interrupted, formation of martensite ceases. These facts are expressed on the typical transformation diagram in Fig. 8.

The mechanism of this transition, in the sense of the movement of atoms in the crystal structure, has also been worked out fairly well. Martensite has the same composition as the parent austenite, and is formed by a process of shear in the austenite crystal. This type of transformation is now commonly referred to as "diffusionless", to distinguish it from the process of nucleation and growth by which pearlite and bainite are produced. The martensite blades are always considerably finer than the grains of the parent austenite. Tempering transforms this

martensite transitional structure to ferrite and expels the carbon atoms.

Strain

Some comment should also be made on Sauveur's fourth question, which concerns the role of strain in the hardening of steel, though we must be careful to define what is meant by strain, since the term has several connotations, some

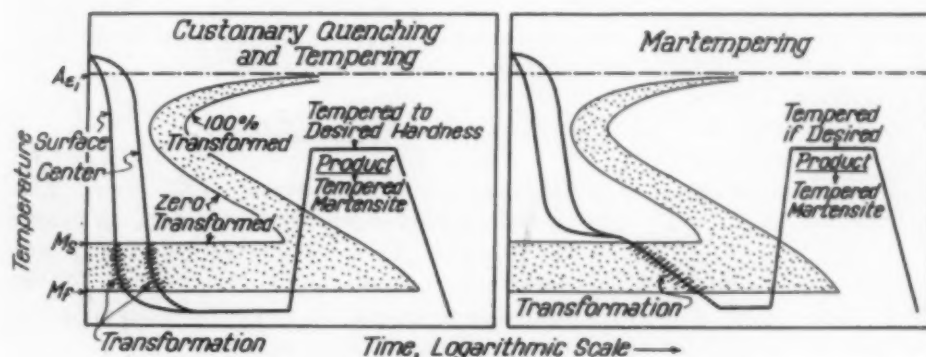


Fig. 9 — Comparison of the Ordinary Quench-and-Temper Hardening Cycle and the Martempering Process

is easy. In this connection it should be noted that the hardness of martensite depends chiefly on carbon content and is largely independent of alloy content. Comparing this with the answers sent to Sauveur in 1926, one realizes that some advances have been made since then; yet I would not claim that what I have just said is much of an improvement over the reply made by McCance that: "The normal alpha iron space lattice is distorted, owing to the presence of the carbon atom, and the hardness of martensite is a consequence of this state of distortion."

Coming now to Sauveur's second question as to the conditions necessary for the formation of martensite and the mechanism of this formation, one again finds substantial progress. It is now recognized, for instance, that, in general, martensite forms only on cooling and then only below a certain maximum temperature, now called the M_s

of which differ today from those in 1926.

If one means strain in the sense of lattice distortion in martensite, then we are fairly certain that strains are significant. Or, if by strain one means shearing in the formation of martensite, then strain is certainly significant.

On the other hand, on reading the replies to Sauveur's 1926 questionnaire, one gains the impression that at that time the idea of strain in hardening arose from the observation that hardened steel often cracked during quenching or later. In this sense, it is now recognized that such strains result either from stresses arising from thermal gradients during quenching or stresses resulting from volume changes accompanying transformation, neither of which is an essential part of the

⁷"Die Martensitkristallisation im Silmbild", by H. J. Wiester, *Zeitschrift für Metallkunde*, V. 24, November 1932, p. 276.

mechanism of hardening. Indeed, the introduction of such processes as martempering has done much to remove the danger of such cracking.

The principle of this process is compared with that of conventional quench-and-temper processes in Fig. 9. It is important to note that these processes differ essentially only in the conditions under which austenite transforms.

In the conventional quench-and-temper process, the piece is quenched so rapidly that no transformation occurs before the M_s temperature is reached. Transformation to martensite then occurs during passage through the martensite range, after which the piece is tempered at a temperature, and for a time, necessary to yield the desired hardness.

In martempering, however, the piece is quenched rapidly to a temperature just above the M_s point, and allowed to come to uniform temperature, thus relieving any stress arising from a thermal gradient within the specimen. It is then cooled relatively slowly through the martensite range so that transformation occurs simultaneously throughout the specimen. Then it is tempered to the desired hardness as before. The prevention of significant thermal stresses by retarded cooling during and after the formation of martensite, and the concurrent partial relief of transformation stresses by self-tempering, usually reduce materially the incidence of cracking.

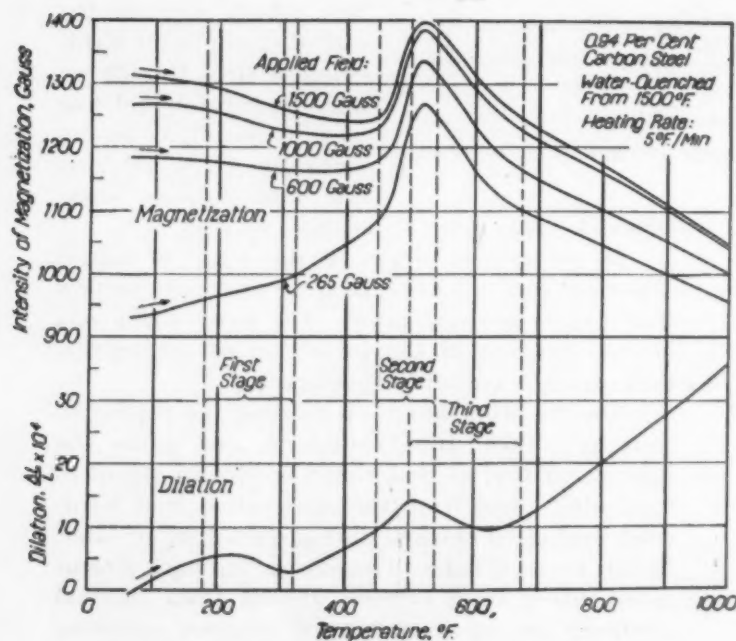


Fig. 10—Magnetization and Dilation Changes on Heating Hardened Plain Carbon Toolsteel. Measurements made at temperature. Note three stages of tempering and the effect of field strength on the magnetic curves. (Antia and Fletcher)

Tempering

Some further mention should be made of the tempering operation itself since this bears on the structure of tempered martensite, which has been mentioned already.

The mechanism of tempering has recently been clarified by Cohen and his associates.⁸ The best evidence now indicates that for carbon steels there are three stages, as shown in Fig. 10:

"In the first stage, which occurs below 400° F., the tetragonal structure transforms to a cubic structure, with the formation of a transitional precipitate, the nature of which is not yet established. Some stress relief also occurs. In the second stage (400 to 600° F.) retained austenite transforms to bainite and more stress relief occurs. In the third stage (500° F. to A_{c1} temperature) the transitional precipitate decomposes with the formation of iron carbide. More stress relief occurs."

Here we have a series of steps that are beginning to be defined in terms of an atomic mechanism instead of a structure as observed under the microscope. Much still remains to be done, yet progress is steady and significant.

Recapitulation

To sum up, since Sauveur's 1926 paper, notable advances have been made, though, as always in research, each step forward raises new questions to be answered. It is now established that it is meaningless to speak of iron carbide molecules existing as such in iron.

The structure of austenite is fairly well established and the significance of the microstructures found in hardened steel has been greatly clarified. The crystal structure of iron present in martensite is fairly well defined and the mechanism of its formation, in the sense of the way in which this structure changes, can be regarded as established. The position of the carbon atoms is also understood, though not completely.

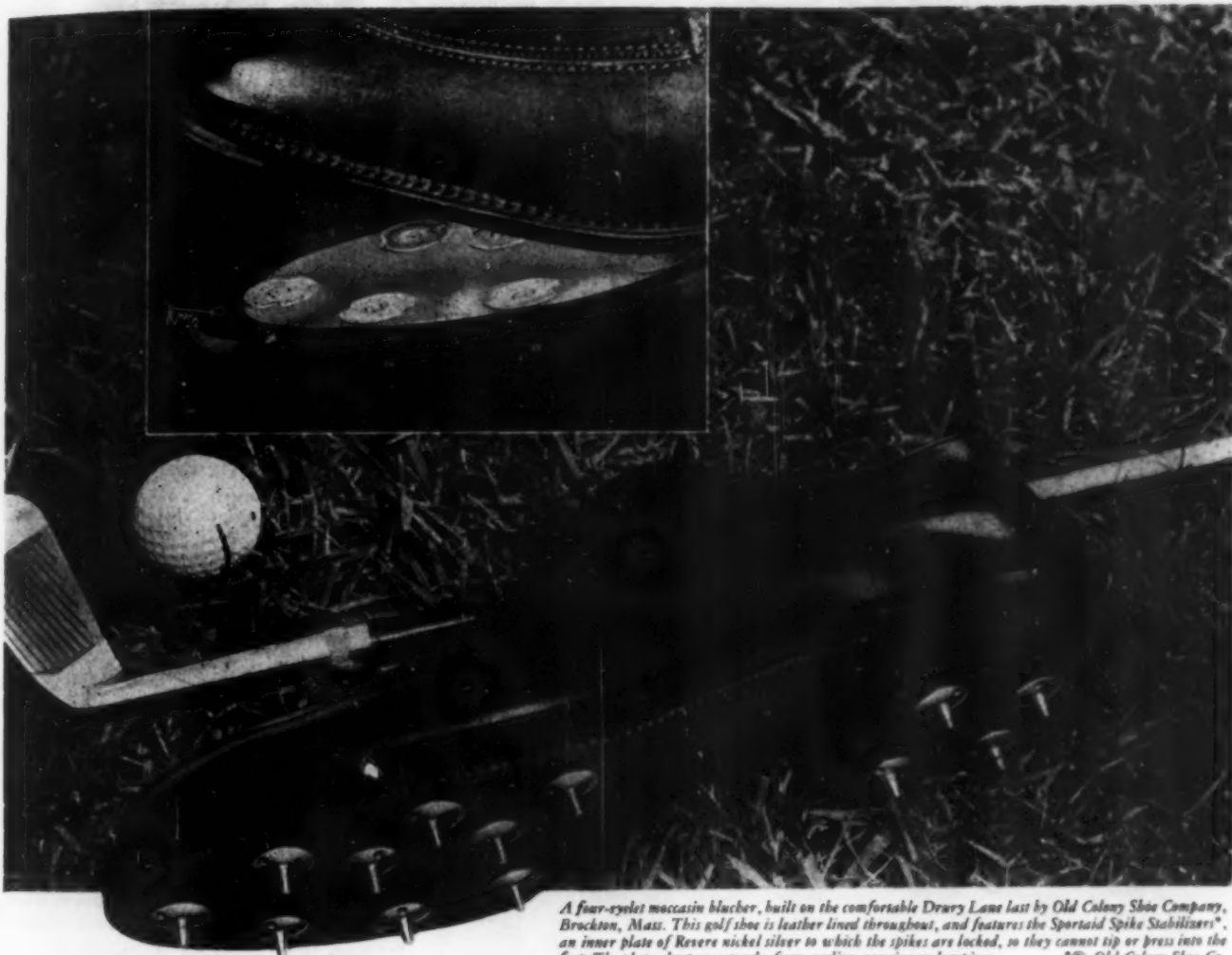
The fundamental cause of the hardness of martensite is still obscure, largely because the concept of hardness itself is not precise.

Further elucidation of the mechanism of the formation of martensite and more complete specification of the transitional stage in tempering are needed.

No doubt some lecturer 25 or 50 years from now will be able to explain these matters to you, but he will probably have a new list of questions that remain unanswered.

⁸"Tempering of Toolsteels", by Morris Cohen. *Metal Progress*, V. 51, May and June, 1947, p. 781, 962.

A CASE IN WHICH AN "EXPENSIVE" METAL PROVES MORE ECONOMICAL AS WELL AS BETTER



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IT is the most natural thing in the world for engineers and purchasing agents to check prices of materials, and when they find that one costs more per pound than another, to conclude, in the absence of other information, that one is more expensive than the other. However, it is often the case that much more than price is needed to determine which is actually the most desirable as well as economical. Take these golf shoes, for example.

Golfers for years were annoyed by spikes that tipped, and dug into the feet instead of the fairway. The Old Colony Shoe Company did something about this. It developed a golf shoe with an inner steel plate to which the spikes are anchored. To prevent rust, the steel was cadmium plated. Golfers went for the shoe. They still do, but what they do not realize is that now

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In making this switch, Old Colony was adhering to its customary policy of making the best shoes it knows how to turn out. Nickel silver costs more per pound than steel, but it was selected because it provides absolute assurance that the plate is equal in quality to the rest of the shoe materials. However, when the cost figures were in, it was discovered, surprisingly, that the nickel silver plates cost less than the steel ones, due to elimination of the plating and associated operations. . . . Naturally, before the final decision was reached to use nickel silver, careful tests were made. Revere cooperated in these and was delighted when the metal proved itself on

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Personals

Having graduated from Cornell University this spring, Thomas A. Foss ☉ has accepted a position in a training program at the Inland Steel Co., South Chicago, Ind.

Charles C. Woolsey, Jr., ☉ has been transferred from the metallurgy section of the U. S. Naval Ordnance Test Station at Pasadena, Calif., to the station at Inyohern, Calif., where he will be acting head of the metallurgy section.

Following the receipt of his doctor of engineering degree from Yale University, Robert Maddin ☉ has been appointed research fellow in metallurgy at Yale.

Arthur R. Constantine ☉, with many years experience in motorcycle, refrigeration and appliance engineering, has joined Indian Motorcycle Co., Springfield, Mass., as head of the engineering division.

Harold P. Weinberg ☉ is now employed as a metallurgical engineer by the Viener Metal Corp., at Richmond, Va.

After receiving his M.S. in metallurgical engineering from Missouri School of Mines in June, J. E. Reynolds ☉ has accepted a position of instructor at his college while continuing graduate studies.

Sidney H. Avner ☉ has joined the staff of the mechanical technology department, New York State Institute of Applied Arts and Sciences, Brooklyn, N. Y.

L. G. Foye ☉ has been appointed engineer in the metallurgical section laboratory of the locomotive and car equipment division, Erie, Pa., works of General Electric Co.

With the purchase of the induction heating division of Budd Co. by the "Tocco" Division of Ohio Crankshaft Co., William K. Ginman ☉, for 11 years with Budd, has been appointed district manager of "Tocco" in the Michigan district office.

A. W. Davis ☉ is now president of the Standard American Engineering Co. of Lyons, Ill.

Joseph C. Vogt ☉, who graduated from Missouri School of Mines and Metallurgy in June 1948, has accepted a position with the American Zinc Co. of Illinois.

Winthrop Towner ☉ has joined the Crown Chemical Corp. of Clinton, Conn., as field engineer in the New England territory.

Formerly with the Submarine Signal Co., Boston, Mass., G. C. Buonagurio ☉ is now a member of the staff of the University of California's Los Alamos Scientific Laboratory, Sandia base branch, Albuquerque, N. M.

Kenneth B. Youngdahl ☉ has joined the Detrex Corp.'s group of engineers and will be connected with the central region office in Detroit.

E. H. Shipley ☉ has recently joined the staff of H. A. Brassert & Co. of New York City as development engineer. He was formerly a research metallurgical engineer with Eaton Mfg. Co.

Following completion of work toward his M.S. degree in metallurgical engineering at Michigan College of Mining and Technology, Robert M. Asselin ☉ has recently accepted a position as research metallurgist with Chain Belt Co., Milwaukee.

Robert A. Schmidt ☉ has left his former position as chief works engineer at the Lafayette, Ind., plant of the Aluminum Co. of America to become the Pittsburgh representative of Standard Alloy Co., Inc., Cleveland.

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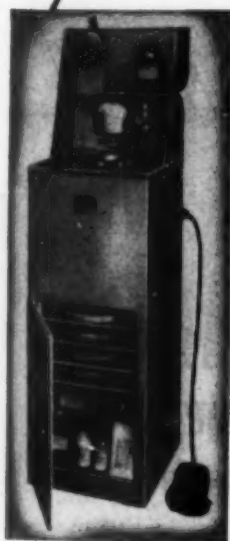
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Personals

T. B. Jefferson, editor of *The Welding Engineer* and for the past eight years secretary-treasurer of the Chicago section of the American Welding Society, has been nominated as a director of the American Welding Society.

Jessop Steel Co., Washington, Pa., announces that Frank B. Rackley has been appointed general manager of sales. Mr. Rackley has been head of stainless steel sales, western area, for Carnegie-Illinois Steel Corp.

After graduating from Pennsylvania State College, Ralph W. Harris has accepted a training position in metallurgy with the Weirton Steel Co., Weirton, W. Va.

Donald F. Davis is now employed as a heat treat metallurgist at the Salisbury Axle Works in Fort Wayne, Ind.

Robert J. Raudebaugh has joined the faculty of Georgia Institute of Technology as professor of metallurgical engineering and as a research metallurgist in the Georgia Tech Engineering Experiment Station.

Joseph Berloldo has started his own engraving business in Malden, Mass.

E. W. Deck, formerly general manager of Trent Tube Mfg. Co., has been appointed manager of the Ithaca, N. Y., plant of the Morse Chain Co.

After 35 years with Wyman-Gordon Co. of Worcester, Mass., C. Fred Milikin has retired from the company.

P. M. Tsai has returned to China where he will work for the Chinese Petroleum Corp. in Shanghai.

Jerome W. Wayno, after completing work for his B.S. at Notre Dame University, has been taking the training program at Detroit transmission division of General Motors Corp. and will be assigned as engineer in the master mechanics section.

Lawrence F. Train, formerly metallurgical engineer in charge of the research and development department, Craig Bit Co., Ltd., North Bay, Ont., will continue as technical consultant of the company while taking on the position of northern representative for the Canada Electric Castings Co., Ltd., Orillia, Ont., and Apco Industries, Ltd., Leaside, Ont.

Charles O. Burgess, for 25 years head of the Steel and Gray Iron Research Laboratories of Union Carbide and Carbon Co., has been appointed technical director of the Gray Iron Founders' Society, Inc., Cleveland, where he will establish a technical department and initiate a long-range program of product improvement, technological development, handbook preparation and technical research.

George W. Motherwell, works manager of Wyman-Gordon Co., Worcester, Mass., has been elected president of the Magnesium Assoc.

Kent Cliff Laboratories, Peekskill, N. Y., announce the appointment of Edward H. Enberg, Jr., in charge of all standardization, and John B. Verrier, Jr., in charge of sales. Both men were associated for many years in similar capacities with Wilson Mechanical Instrument Co., Inc.

The American Society for Quality Control has elected Ralph E. Warham, vice-president and director of National Photocolor Corp. of New York, as president for the coming year; W. R. Weaver, of Republic Steel Corp. of Cleveland, has been elected vice-president; S. Collier, of Johns Manville Corp., New York, is executive secretary.

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Personals

After graduating from Carnegie Institute of Technology in June 1948, **John O' Meara** ☉ has joined the American Manganese Steel Div. of American Brake Shoe Co. at St. Louis.

J. D. Harvey ☉ has been appointed assistant to the president of Export Traders Co. of New York.

The U. S. Atomic Energy Commission announces the appointment of **Evan Frank Wilson** ☉ as assistant director of the division of raw materials. Mr. Wilson, prior to this appointment, was chief metallurgist for the Babcock and Wilcox Co., Barberton, Ohio.

Claire C. Balke ☉, formerly with the Fansteel Metallurgical Corp. and Los Alamos Atomic Bomb Laboratory, has recently accepted the position of director of research at Roberts & Mander Corp., Hatboro, Pa.

L & S Bearing Co., Oklahoma City, Okla., announces that **Paul A. Cushman** ☉ has joined its organization. Dr. Cushman was formerly metallurgist and test engineer of McGill Mfg. Co., Valparaiso, Ind.

Karl L. Fetzters ☉, special metallurgist of the Youngstown Sheet and Tube Co., and **J. L. Mauthe**, vice-president of the same company, were awarded the American Iron and Steel Institute Medal for their paper "The Mineralogy of Basic Open Hearth Slags".

The International Nickel Co. announces the appointment of **John W. Crossett** ☉, formerly with the Chicago, Milwaukee, St. Paul and Pacific Railroad, as a member of the development and research division. Mr. Crossett will follow railroad development work.

Western New York Section of the American Chemical Society has awarded the Jacob F. Schoellkopf Medal for 1948 to **Marvin J. Udy** ☉, consulting engineer of Niagara Falls, N. Y., whose many patents include the Udylyte process.

American Brake Shoe Co. has promoted **Raymond H. Schaefer** ☉ to the position of director of research and development. Mr. Schaefer has been with the company since 1940 and has been most recently chief metallurgist in charge of metallurgical research and the company's experimental foundry.

Edward D. Thompson ☉, formerly assistant to the president at Ontario Mfg. Co., is now works manager of the Badger Meter Mfg. Co., Milwaukee.

James K. Perrin ☉, who graduated from Rensselaer Polytechnic Institute in June, has joined the sales department of Bethlehem Steel Co., Bethlehem, Pa.

E. J. Korda ☉ has been employed as metallurgist with the Wright Aeronautical Corp., Wood-Ridge, N. J.

Babcock & Wilcox Tube Co., Beaver Falls, Pa., announces that **William J. Thomas** ☉ has been appointed general manager. He has been with Babcock & Wilcox since 1932, most recently as assistant general sales manager.

Evan N. Davidenko ☉ has recently joined the U. S. Naval Torpedo Station, Newport, R. I., in the capacity of materials engineer in the research department.

Bradley Higgins ☉, formerly assistant plant engineer at the Worcester Pressed Steel Co., has been appointed assistant to the president of the Livingstone Engineering Co., Worcester, Mass.



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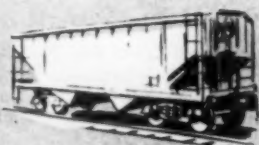
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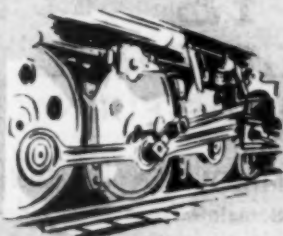
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Bel cranks, radius bars, and other vital parts of high-speed locomotives that must be strong and tough, are made of manganese-vanadium steel of medium-carbon content.



Crankshaft forgings, which must have exceptionally high strength, are made of steel containing vanadium.

Low-carbon, manganese-vanadium steel has high strength and ductility in the as-rolled condition. This steel also has particularly good weldability because of the fine grain imparted by vanadium, and its low carbon content. Welds in this steel show little tendency toward air-hardening, and retain strength and ductility almost equal to that of the original plate.

Following is a typical analysis for low-carbon, manganese-vanadium steel plate and rolled products. This composition is suitable for many applications where a low-alloy, high-strength steel is required. Note the excellent properties of this steel.

TYPICAL MANGANESE-VANADIUM STEEL ANALYSIS

Vanadium	0.08 to 0.12%
Carbon	0.11 to 0.16%
Manganese	1.20 to 1.45%
Silicon	0.15 to 0.30%

AVERAGE PROPERTIES

Tensile Strength	85,000 to 95,000 psi.
Yield Point	55,000 to 72,000 psi.
Elongation in 2 in.	18 to 27%
Reduction of Area	50 to 70%

Our metallurgists have had a great deal of experience over the years in the application of alloy steels. They will gladly help you select the right steel for a particular job. If you wish assistance, consult our Technical Service Department. There is no charge for this service.

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Personals

C. F. Johnson ☉, formerly with Watson-Stillman Co., has become associated with Manning, Maxwell & Moore, Inc., of Bridgeport, Conn., as special representative of the company in Houston, Tex.

Carnegie-Illinois Steel Corp. announces that R. F. Miller ☉ has been appointed assistant to the vice-president of the research and technology department. Dr. Miller began his service with U. S. Steel Corp. at the Kearny, N. J., laboratories in 1936, and was appointed development engineer in stainless and alloy steels for the department of research and technology in 1943.

James L. Erickson ☉ has been appointed regional sales representative in southern Ohio and Indiana for the Production Die Cast Co., Grand Rapids, Mich.

Bani R. Banerjee ☉ is visiting India during the summer of 1948, on leave from the Illinois Institute of Technology, Chicago, where he plans to resume his duties as a member of the faculty in the department of metallurgical engineering in the fall.

Dana J. Demorest ☉, for 33 years a member of the faculty of Ohio State University, will retire as chairman of the department of metallurgy on Sept. 1, 1948, although he will continue his teaching duties for a few more years.

Tube Turns, Inc., Louisville, Ky., announces that John G. Seiler ☉ has been elected executive vice-president. He was previously sales manager of the company.

T. F. McCormick ☉ has been transferred by the Aluminum Co. of America from the Lafayette works to the Pittsburgh office where he will be a staff metallurgist.

Joseph W. Pitts ☉ has recently joined the National Bureau of Standards, Washington, D. C., in the enameled metals section of the Mineral Products Division.

W. D. Jeffries ☉ has been appointed sales and service representative for cyanides and heat treating salts for E. I. du Pont de Nemours & Co. in the Chicago district.

After receiving his M.Sc. from Ohio State University, Paul R. Totten ☉ has been employed at the Thomas Steel Co., Warren, Ohio, as a metallurgist specializing in heat treatment.

Structural Strength of the Welded Joint*

DURING World War II, problems arose as a result of the expanded use of welding, particularly when applied to rigid, massive structures, when steels were used having greater tensile strength and hardenability than mild steel, and when the welded structures had to be used at low temperature.

The results of several recent investigations indicate that, under many service conditions, the performance of a welded joint, even when made in accordance with the best accepted practices, is far from satisfactory and can be improved considerably if and when proper research points the way. Two major examples of such investigations were discussed.

The first example was the investigation, under Navy sponsorship, of the structural failures of Liberty ships. One phase (*Cont. on p. 218*)

*Abstracted from the 1947 Adams Lecture of the American Welding Society, by G. S. Mikhlapov. *Journal of the American Welding Society*, V. 27, No. 3, 1948, p. 193-206.

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IN ADDITION TO THESE DISTRIBUTORS, local dealers in industrial and agricultural areas handle Stoodly products. For the name of your local dealer, write or phone the distributor nearest you.



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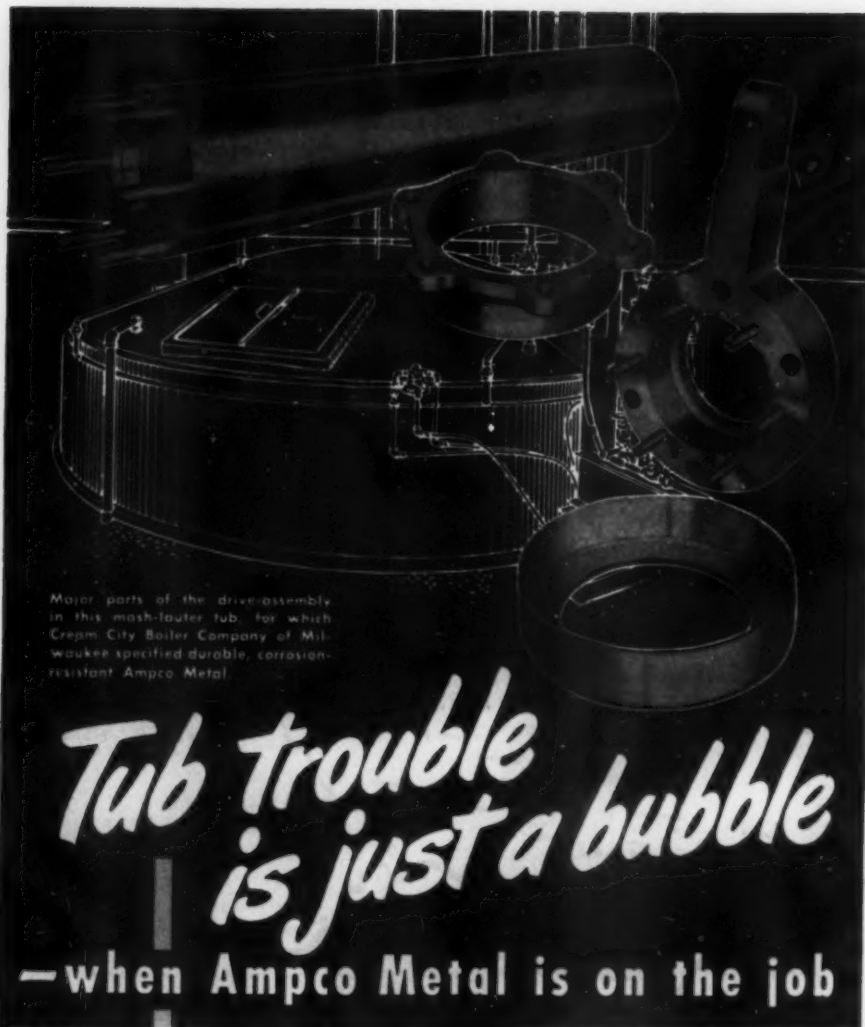
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Tub trouble is just a bubble —when Ampco Metal is on the job

That's why corrosion- and wear-resistant Ampco Metal is used for bearings and other critical parts in this mash and lauter tub

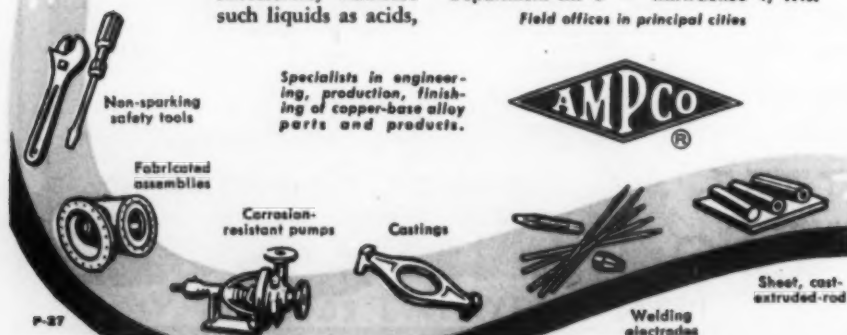
Critical parts made of Ampco Metal are an assurance of *long and trouble-free service, low maintenance and replacement costs*. Ampco Metal gives you many important qualities not found in other anti-acid metals: High tensile strength; good ductility; less weight; hardness to resist squashing, wear, impact, and fatigue; good bearing qualities. Ampco's aluminum bronze also resists corrosion, erosion, and cavitation—successfully handles such liquids as acids,

alkaline solutions, sea water, mine waters, petroleum sludge, hot brine, and food-product liquors. Whatever your process problem may be, get in touch with us. Our engineers can save you time and money by helping you adapt Ampco Metal, or assemblies of Ampco Metal and alloys, to your requirements.

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Structural Strength of the Welded Joint

(From p. 216) of this investigation dealt with tests of specimens reproducing full-scale ship sections—for example, the corners of hatches. These tests indicated that a random change in the welding procedure (preheating the steel at 400° F.) was of greater benefit than a carefully planned change in the chemical composition of the steel.

The second example was the investigation of portions of simple butt-welded steel plates by subjecting them to high-velocity impact, normal to the plane of the plate. (These results were first described by W. A. Snelling and W. O. Snelling in O.S.R.D. and N.R.C. reports, in 1945 and 1946.) This impact was produced by a detonating wave traveling through a column of explosive. The specimen being tested was a 12x12 or 18x18-in. prime or welded plate, ½ to 1½ in. thick, and was supported horizontally on a flat base. A measured quantity of explosive was placed on the portion of the specimen to be tested, and the detonation of the explosive produced an impact of measurable energy and a condition of triaxial tension in the plate. Because of the high rate of strain during this test, the conditions were probably equivalent to triaxial tension at low temperature.

In this direct-explosive test, unwelded notch-tough plates deform considerably before failing by a single or Y-shaped crack, but unwelded notch-sensitive steels deform only slightly and shatter into many pieces.

Under most conventional tests, the performance of a butt welded plate specimen would be virtually indistinguishable from the performance of the prime plate. However, in the direct-explosive test, the performance of a welded specimen ranged from 25 to 90% of that of the component prime plate, depending on the qualities of the plate and on the welding procedure used. The most common performance of welded plate was approximately 50% that of the prime plate.

According to a tabular summary of data on prime and welded plate, improvement in the prime plate raised the energy necessary to fracture the plate from 465 units to 600 units. However, welding the best plate reduced the energy to a figure of 350 units after welding.

(Continued on p. 220)

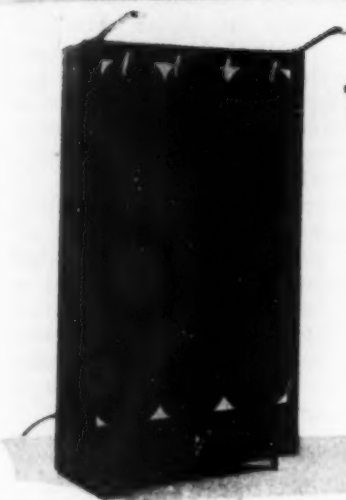
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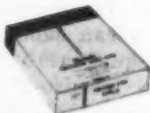
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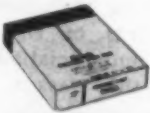
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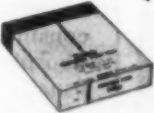
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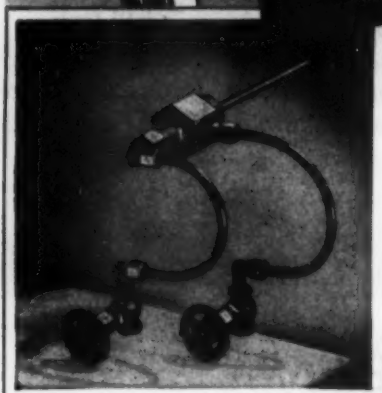
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Structural Strength of the Welded Joint

(Starts on p. 216)

One factor that may be responsible for the apparent inferiority of the welded joint to the parent plate is the difference in the metallurgical structures of weld metal, heat-affected zone and parent plate. Some of these structures are unsatisfactory in resistance to fracture and deformation under combined stresses. The conventional tensile test, being substantially unidirectional, is not a reliable guide to the performance of these structures when combined stresses are present in a welded joint.

A second factor is the effect of gas composition of the arc-shielding atmosphere. Some of the most spectacular improvements in the performance of welded joints have resulted from changes in the arc atmosphere, but there is slight understanding of the chemical or physical principles involved. Undoubtedly dissolved gases, such as hydrogen, oxygen, and possibly nitrogen, affect the properties of the weld area.

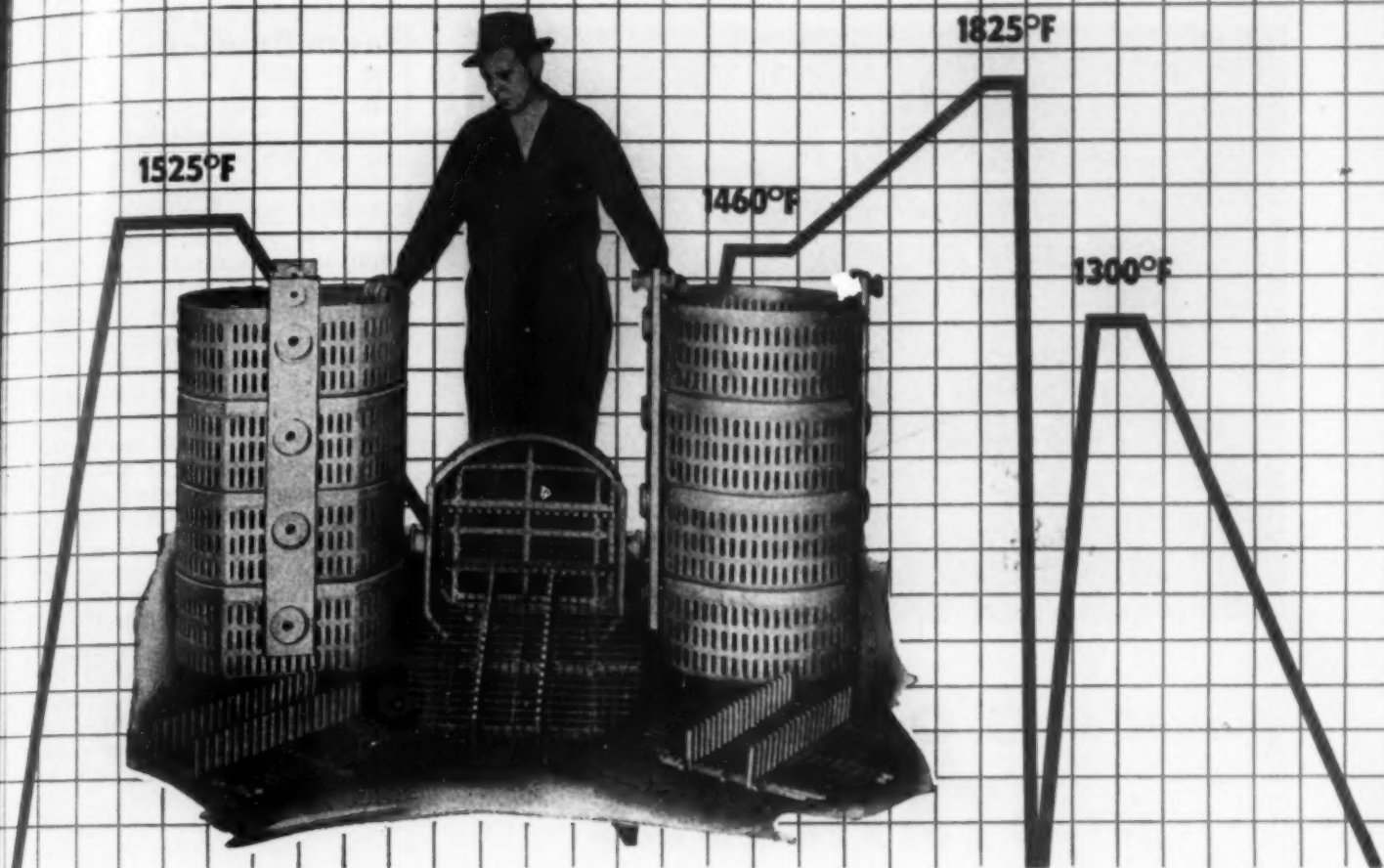
Gas in Bronzes*

THE AUTHOR of this paper did some pioneering work on the degassing of bronzes and reported his findings in 1940 and 1941. He used then a degassing flux containing various amounts of copper oxide (CuO) plus clean sand and borax taken in equal amounts. Essentially his flux consisted of a fluid mixture of silicates of copper with copper borates and sodium borate.

W. A. Baker re-examined the process in 1944 and concluded that it works satisfactorily on nearly pure binary bronzes, but produces no results with those that contain considerable amounts of zinc or phosphorus—as commercial alloys usually do. For this reason the present author reinvestigated the question in 1947.

The first step was to prepare 20 alloys from virgin metals, copper and tin, under the oxidizing flux and to add lead, zinc or phosphorus later on. (Cont. on p. 222)

*Abstract of "The Control of Gas Content During the Melting of Phosphor Bronzes, Gun Metals, and Leaded Bronzes", by W. T. Pell-Walpole. *Metallurgia*, January 1948, p. 119.



You can give NICHROME* terrific punishment ...and still get low heat-hour costs!

Here, for example, is what we mean: These baskets and fixtures, used for hardening stainless steel impeller blades during heat treating operations, *must stay on the job* despite punishing cycles and high-rate quenching.

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The superb heat and corrosion-resistant properties of Nichrome, assuring long life and dependable service under such punishing conditions, have enabled these baskets and fixtures to remain in operation for over a year without any need for repair. In addition, the lighter construction made possible by Nichrome has reduced deadweight—resulting in higher heat transfer and less heat consumption. Result: Low heat-hour costs.

If your heat-treating problem is as tough as this one, and you would like better results, Nichrome is most probably the the right answer; if it is of the "common or garden variety", Nichrome will give you phenomenally more efficient, economical and lasting service.



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Stainless Steels Exclusively

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Gas in Bronzes

(Cont. from p. 220) Specimens so produced were considered as standards of density, cleanliness and physical characteristics. The physical values were quite high, as the metal was cast into vertical chill molds at a rate insuring minimum shrinkage, but the question remains whether the porosity was completely eliminated. (A phosphorus bronze that might show a theoretical density of 8.70 had 8.75; a high leaded bronze has shown 9.17 against a theoretical 9.23. Volume contraction due to the formation of solid solutions is usually somewhat greater.)

Next the author proceeded to prepare highly gassed scrap metal ingots by melting up scrap and letting it run through a dozzle lined with red sand baked at 100° C. The resulting gassy metal was used to test the efficiency of the CuO flux. The latter was taken in amounts of 3 and 6% of the weight of the metal, and its CuO content varied from 0.08 to 0.67 of the total. It was found that:

1. Phosphor bronzes containing no zinc could be degassed rapidly with a flux containing 33% CuO. The resulting metal had a high ultimate tensile strength and a high, if variable, elongation. Ordinary melting in an oxidizing atmosphere gave slightly inferior density and ultimate, but the elongations were much lower. The loss of phosphorus was slight and easily remediable.

2. High phosphor bronzes containing 1.5% P could be degassed completely using the same flux as above. The loss of phosphorus was greater, but by no means excessive, and could be remedied with a small addition.

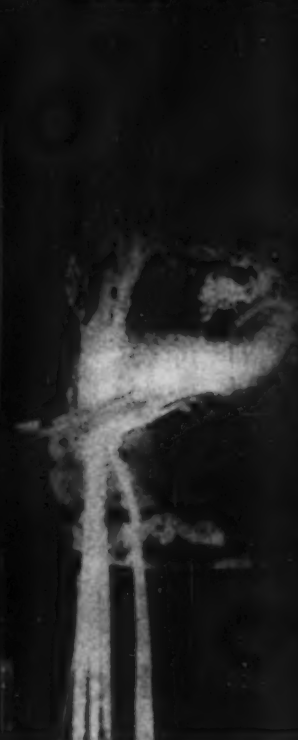
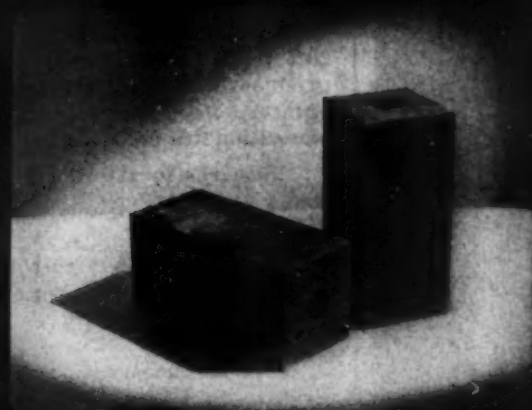
3. Gassy scrap of high phosphor bronze can be degassed just as effectively and without losing much phosphorus, but the flux must contain 50% CuO.

4. Highly gassed admiralty gun metal (88 Cu, 10 Sn, 2 Zn) can be degassed quite effectively using 50% copper flux; not more than 0.5% Sn and 0.5% Zn need be added to make good the losses, if any. Melting under oxidizing conditions produces a metal of fairly high density, but an inferior tensile strength and a much inferior elongation.

5. Gassed alloys of the 88-8-4 type are not helped by the copper oxide flux to any greater extent than by an ordinary oxidizing atmosphere. (Cont. on p. 224)

CRYSTOLON Slag Hole Blocks

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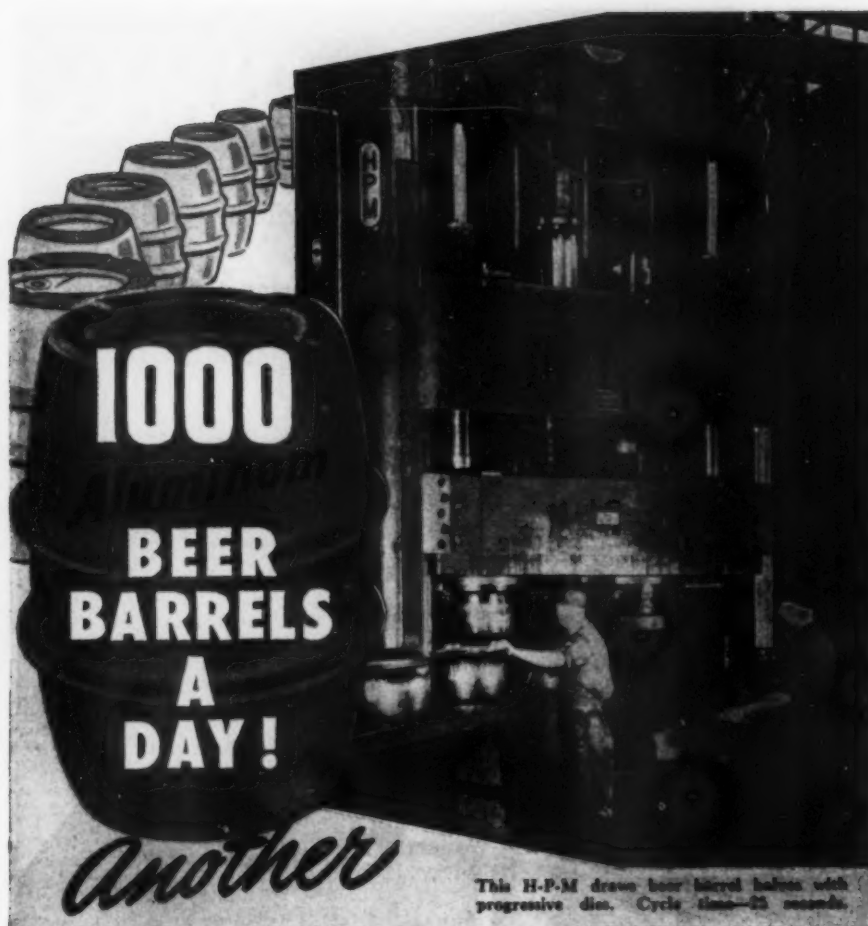


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CRYSTOLON blocks resist all slag action either by corrosion or erosion. Consequently the hole size is maintained for a longer period of time, giving better control of the flow. These rugged slag hole blocks are highly refractory and will neither soften nor spall at temperatures up to 1650°C.



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Metal Working Presses



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Gas in Bronzes

(Starts on p. 220)

6. The 85-5-5-5 bronze ("red metal") is not benefited by the CuO-flux to any substantial extent, in comparison to melting in an oxidizing atmosphere.

7. In leaded bronzes (10 and 20% lead) the flux with 50% CuO produces a metal of higher density, but the effects upon strength and elongation are none too striking.

Remarks by the Abstractor

An interesting point is that the characteristics of the upper test piece were always higher than of the lower one. For instance:

	DENSITY	ULTIMATE	ELONGATION
High-Zn gun metal			
Upper	8.80	51,000 psi.	41%
Lower	8.80	45,300	21
88-10-2			
Upper	8.81	51,300	17
Lower	8.78	42,800	8
11 Sn, 1.5 P			
Upper	8.62	64,000	8
Lower	8.60	53,100	3

and so on. The following reasons might be advanced:

1. Upper test bar was poured from the lower layers in the small crucible and these were lower in gas than the upper layers.

2. Upper layer of the metal in the crucible carried larger amounts of solid impurities.

3. The lower part of the cast bar cooled too rapidly in the ingot mold and the amount of the delta constituent was greater, thus reducing the ductility.

It is unfortunate that no stress-strain diagrams were taken and no Brinell figures are given. The micrographs also are not too plentiful.

M. G. C.

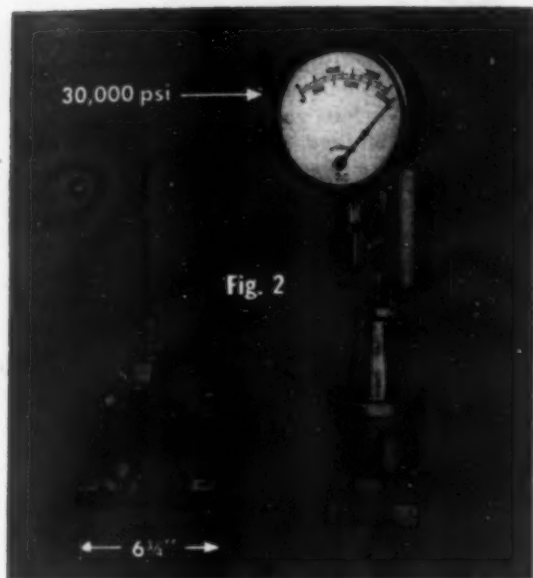
Magnesium for Cathodic Protection*

THE PAPER covers the results of a research program designed to determine the feasibility of using magnesium anodes for the cathodic protection of steel in sea water. The exposure tests were made at Kure Beach, N. C.

The first part of the paper deals with the anodic performance of various magnesium (To p. 226)

*Abstracted from "The Cathodic Protection of Steel in Sea Water With Magnesium Anodes", by H. A. Humble. Paper presented before the National Association of Corrosion Engineers, April 1948.

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Magnesium for Cathodic Protection

(Continued from p. 224) alloys. Cell magnesium and magnesium alloys AZ63, AZ31X and AZ61X were cast as cylinders 4 in. in diameter by 20 in. long, and these specimens were suspended in plastic frames and placed 4 ft. below mean low tide. Sixteen specimens of each alloy were coupled electrically to the sheet steel piling walls of the test basin and four served as uncoupled controls. Recording potentiometers were used to measure and record the flow of current. Various current densities were obtained by installing fixed resistors in series. Most of the tests were run for three months.

The magnesium anodes were satisfactory for the cathodic protection of steel in sea water. Solution potentials of -1.5 volts (versus saturated calomel electrode) were observed; these are virtually independent of time and magnitude of current flow. Recoveries of 500 to 600 amp-hr. per lb. of metal consumed were realized.

The second part of the paper deals with the current necessary for cathodic protection. The current required changed rapidly with time after the application of a protective current. If high current densities sufficient for immediate protection are applied, this current will be too high as time progresses. If current densities equivalent to equilibrium conditions are applied, substantial corrosion may occur for some time (perhaps several years) before complete control of corrosion is obtained. The best method appears to consist in a high initial applied current density that is subsequently lowered. The advantages of this method are: (a) Immediate protection is obtained. (b) The high initial current densities precipitate a calcareous coating over the surface of the cathode, and this will stifle corrosion. This coating also reduces the current required. (c) Total current requirements are lower for extended exposure times.

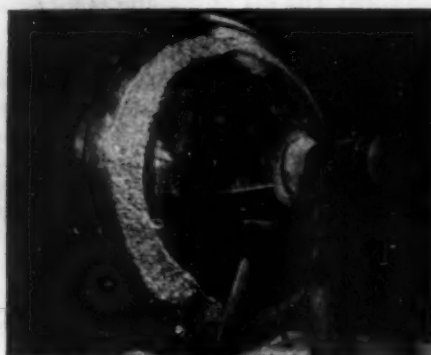
Sandblasted and rusted killed steel plates were used and coupled with magnesium anodes. For the sandblasted steel more than 10 ma. (milliamperes) per sq.ft. is required for initial protection but protection may eventually be achieved by a fixed current density of about 6 ma. per sq.ft. The rusted steel can be protected with a slightly lower current density.

(Continued on p. 228)

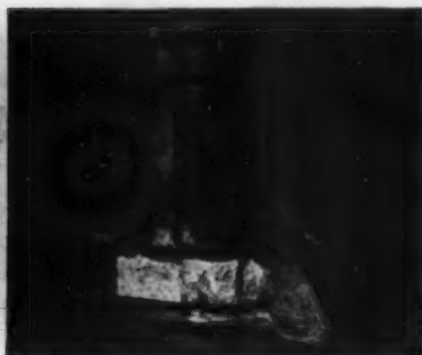
Replacement of this \$1,400 ring gear would have taken from six months to a year. The badly worn teeth were built-up by bronze-welding and the gear returned to service in just a few days at half the cost of a new one.

Keeping the "wheels" going 'round

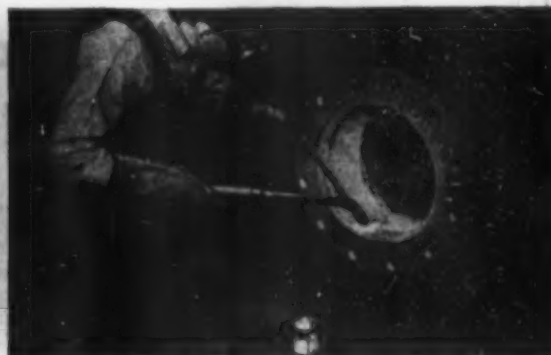
The repair of vast quantities of equipment by oxy-acetylene methods is of course routine for plant maintenance crews. It is for the special job, however, that the LINDE serviceman's supervision and work proves so valuable and gives assurance of success. This skilled, specialized assistance is always available to LINDE customers. Just phone the nearest LINDE office.



Bronze-welding this cast steel cone crusher head saved \$1,000. The crack, which ran completely around the head for a distance of $9\frac{1}{2}$ ft., extended through the thickness of the casting in several places. It was veed out by flame-gouging.



This cast iron steam hammer cylinder weighs 4,000 lb. Two large cracks, one on each side of the cylinder wall, were bronze-welded in only 14 hours. A new casting would have taken 16 weeks to obtain and would have cost more than 10 times as much.



Flanges are quickly joined to cast iron pipe sections by bronze-welding. LINDE supplies several bronze rods to meet varying service requirements.

Linde

Bronze-welding effected a considerable saving of cost and time when four spokes of this huge cast iron pulp-chipper wheel was cracked at the hub.

The word "Linde" is a registered trade-mark of The Linde Air Products Company.

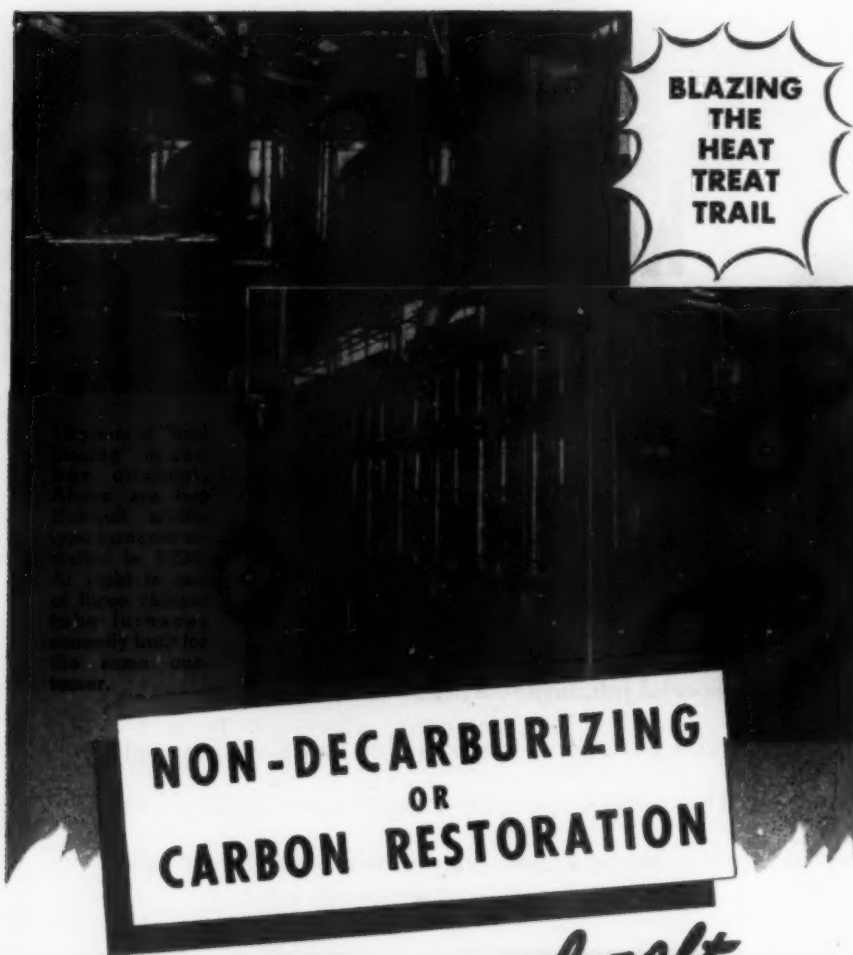


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Magnesium for Cathodic Protection

(Starts on p. 224)

The rusted specimens were exposed for three months before the protective current was applied. The difference in weight loss between the sandblasted and rusted plates is attributed to the presence of the coatings deposited by the corrosion process and the accompanying partial polarization of the local cathodic areas on the rusted plates at the time of coupling.

The most outstanding characteristic of sea water corrosion is the tendency for calcareous deposits to form on cathode areas. High current densities increase the pH of the water film at the cathode and thus favor deposition of these coatings. Compositions of the coatings deposited under different current densities show high calcium content for low current densities and high magnesium content for high current densities. The protective action of these coatings is believed to be caused by the following: (a) The coatings serve as a barrier to oxygen or other depolarizers. (b) They increase the internal resistance of the local corrosion cells. (c) The pH of the film is increased above that of normal sea water.

Current densities as low as 3 ma. per sq.ft. afford protection if high initial current density (50 ma. per sq.ft.) is used to obtain immediate polarization. This permits the use of considerably smaller permanent anode installations, saving approximately 40% in current.

Electroplate on Magnesium*

SUCCESSFUL and adherent electroplates over magnesium alloy shapes in any commercial form require first the preparation of a "completely homogeneous reactive surface" on which is placed a flash of zinc from a process (available from Dow Chemical Co. under license agreement) developed by Herbert K. DeLong. After the zinc film is deposited, a copper layer is then plated on from a typical Rochelle salt bath. This copper strike, about 0.0004 in. thick, forms the basis for the final coating, such as nickel, chromium, silver or gold, by ordinary methods. (To p. 230)

*Abstract of a paper before March 1948 meeting of the Magnesium Assoc. by William Loose.



ELECTRONIC HEATERS ON THE JOB: LATHE-BED HARDENING

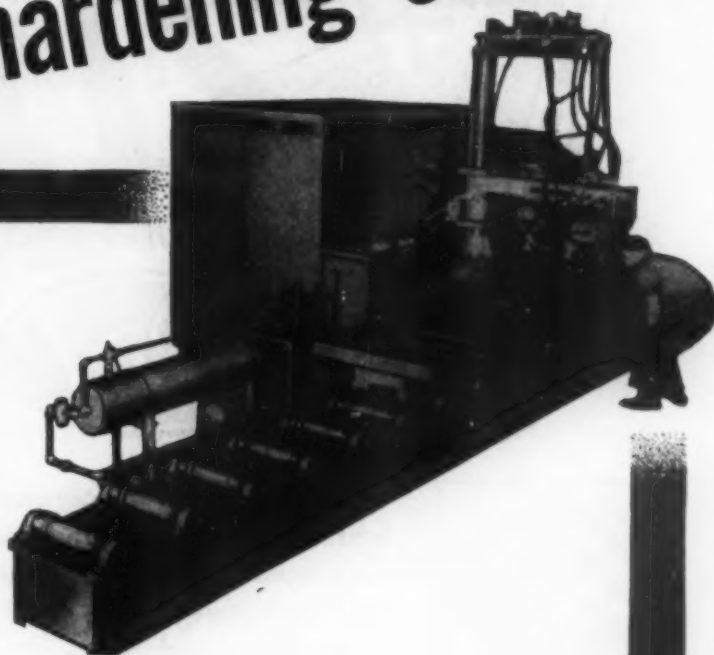
**uniform hardness
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is now being given to machine-tool lathes at the Hendey Machine Company, Torrington, Conn. Thanks to the uniform hardness made possible by a G-E electronic induction heater, precision surfaces of lathe-bed ways remain "mirror-smooth" far beyond previous life expectancy . . . are less vulnerable to precision-destroying wear and accidental damage.

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Net result: a better product through induction heating.



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Whether your product involves brazing, soldering, hardening, or annealing, be sure to get in touch with the Heating Specialist in the nearest G-E Office. His suggestions are very likely to result in higher production, lower cost, and better products, as they have for many other manufacturers. In the meantime, send for free bulletin GES-3290, "The How and What of Electronic Induction Heating." Sect. 675-178, Apparatus Department, General Electric Company, Schenectady 5, N.Y.

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Electroplate on Magnesium

(Continued from p. 228)

Surface cleaning varies with the nature of the piece. Grease is removed by solvents followed by cathodic cleaning in ordinary alkaline cleaners. Wrought products are first pickled in 20% acetic acid plus 5% sodium nitrate. Cast products are cleaned in 75% phosphoric acid solution. After pickling and buffing, surfaces must be "activated". For alloys containing aluminum or zinc this is done in 20% $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$. For other alloys 1% acetic acid is used. Photo-engraving plates are cleaned in 20% chromic acid followed by 15% HF solution.

The zinc strike is then plated on in about 4 min. by immersion and agitation in the following bath contained in stainless steel tanks at 175° F.:

12% Tetra sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$

4% Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$

1% Potassium fluoride, $\text{KF} \cdot 2\text{H}_2\text{O}$

0.5% Potassium carbonate, K_2CO_3

This solution is made up in iron-free water to pH of 10.3.

Hydrogen Absorbed by Steel From Acid*

WHEN a piece of steel is immersed in an acid solution with which it reacts to liberate hydrogen, some of the hydrogen enters into the steel, or even passes through it. As the presence of a large concentration of hydrogen may have a significant influence on the properties of steel, a knowledge of the processes by which it diffuses in or out is desirable. The experiments described were of two principal types, one designed to measure the permeability of the steel to hydrogen and the other to measure saturation concentration and diffusivity of hydrogen in steel.

Detailed information was included about the experimental procedure and apparatus used in conducting the diaphragm-type measurements and the solubility and diffusivity determinations. The precautions necessary (To p. 232)

*Abstracted from "The Behavior of Steel During and After Immersion in Acid", by L. S. Darken and R. P. Smith. Paper presented before the National Association of Corrosion Engineers, April 1948.

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Select THE ALLOY THAT DOES YOUR JOB BEST

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 FLATS $\frac{1}{8}$ " x 1" to $1\frac{1}{2}$ " x $2\frac{1}{2}$ "
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 PIPE $\frac{1}{8}$ " I.P.S. to 2" I.P.S.
 Pipes larger than 2" formed and welded to order
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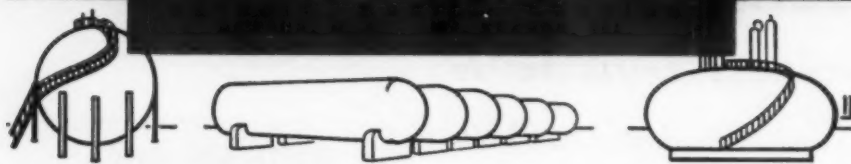
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Hydrogen Absorbed by Steel From Acid

(Continued from p. 230)

for successful operation also were discussed in detail.

It was determined by experiment that very seldom did an 18-hr. extraction at 340° F. fail to yield at least 90% of the hydrogen that could be extracted in vacuum at temperatures up to 1475° F. Water present on the surface of the sample did not give fictitious results. Reproducible results were obtained under like conditions of test. However, depletion of the acid used in a test caused slight discrepancies of less than 0.01 cc. per g.

Tests were made in order to determine the effect of specimen size on permeability and diffusivity. The variation in permeability is comparable with the reproducibility of the measurements, although not experimentally equal. Hydrogen absorbed was proved to be truly absorbed into the interior of a steel specimen; the experimental error caused by surface adsorption is small. Other tests showed that hydrogen is not diffused linearly from one side to the other when the specimen is half-exposed, and is approximately 80% that of the fully-exposed specimen. The rate of evolution of absorbed hydrogen was slower than the rate of absorption, for a given steel specimen.

Experiments were conducted to determine the effect of solution conditions on solubility and permeability. As the pH of the solution increased, both the permeability and diffusivity decreased. In a similar test it was found that the permeability doubled for each 36° F. increase in temperature. The effect of using inhibitors was marked; both inhibitors tested reduced the permeability to a low value.

Cold work greatly increases the ability of steel to absorb hydrogen. The saturation value is very small for hot rolled steel but increases markedly with cold work; the extent of this increase varies from steel to steel. However, the calculated permeability was found to be unaffected by cold work. The mean deviation of the calculated permeability was always less than 10%.

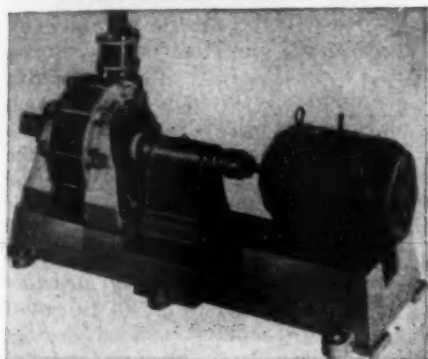
The saturation value is decreased slightly by long annealing of cold worked steel but the rate of absorption is decreased considerably. Tempering decreases the solubility slightly and the permeability markedly. (Continued on p. 234)



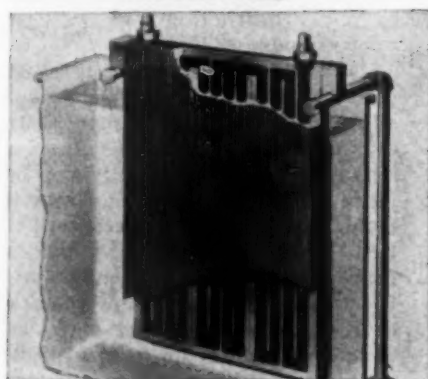
"Karbate" Sectional Cascade Cooler



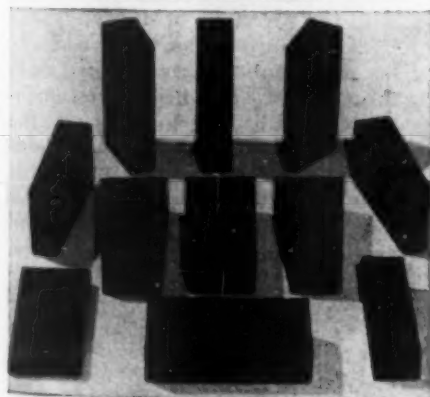
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"National" carbon brick is now extensively used for lining tanks that handle corrosive solutions — particularly nitric-hydrofluoric.

For more details on metal-cleaning systems of standard "Karbate" brand Impervious Graphite units and "National" carbon brick, write to National Carbon Company, Inc., Dept. MP.

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Hydrogen Absorbed by Steel From Acid

(Starts on p. 230)

The observed phenomena are interpreted to mean that only a small fraction of the hydrogen absorbed by cold worked steel is interstitial and the remainder is trapped in imperfections in the crystal structure. No evidence of molecularly absorbed hydrogen was found.

Electron Diffraction of Corrosion Films*

ONE of the most interesting and instructive uses of electron diffraction and electron microscopy has been the study of the protective or nonprotective corrosion films on metals and alloys. The use of such refined methods results from the fact that in the protective range the corrosion films are of the order of 10 to 10,000 Å in thickness. The study of the crystal size, crystal structure and secondary structure of films in this range of thickness can be prosecuted only by electron diffraction and electron microscopy. Thicker films can be studied by X-ray diffraction and the light microscope.

Although the reaction involved in the dry oxidation of metals and alloys may be simpler than many other corrosion reactions from a chemical point of view, it may be more complex from an experimental point of view, because it is best studied in the electron diffraction camera at high temperature. Electron diffraction is applicable to the processes of wet corrosion if the reaction is uniform and pitting does not occur. However, this paper was concerned primarily with the reactions of dry oxidation.

The study of surface reactions in dry oxidation is divided into three parts. The first part is concerned with the kinetics of the reaction processes or rate of reaction and the manner in which this rate is influenced by time, temperature, pressure, surface factors and chemical factors in the atmosphere.

(Continued on p. 236)

*Abstracted from "The Application of Electron Diffraction Techniques to the Study of Corrosion Processes", by E. A. Gulbransen. Paper presented before the National Association of Corrosion Engineers, April 1948.



FOLKS, they're just coming in too fast—and we do mean *orders*! In anything like normal times, we'd be awfully happy to have you pitch your order down our alley. Our past averages speak for themselves.

But *now*—well, honestly fellows—there are too many pitchers on that mound. We're in there swinging as hard as we can but we can only manage to get hold of a few. And there just aren't any pinch-hitters on the bench to help us out.

From your seat, our batting average no doubt looks weak at the present time. But we're doing the best we can and we're hitting 'em safe when we can get hold of 'em.

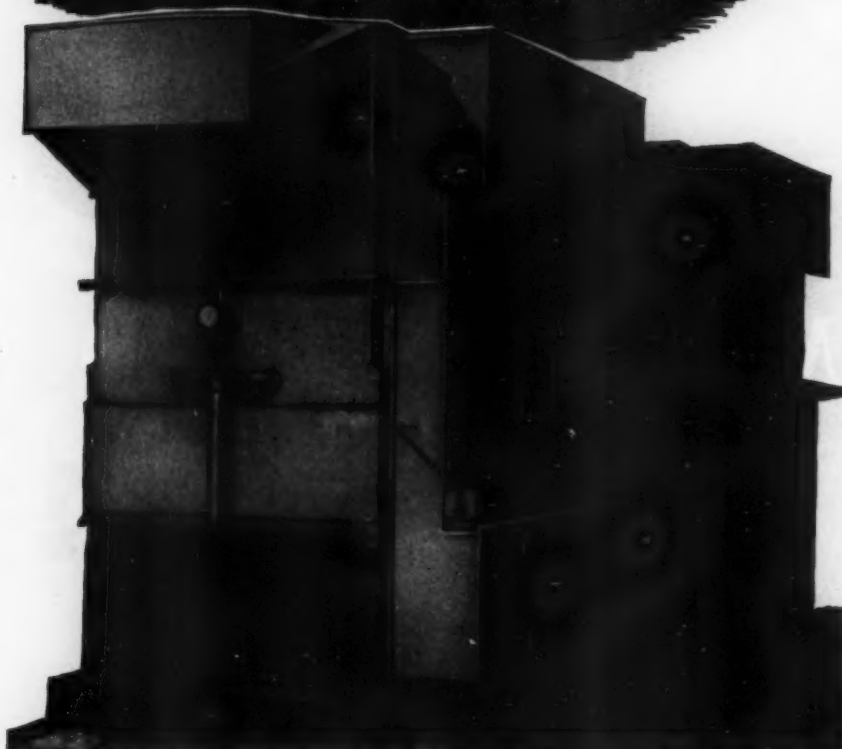
We're asking you to stick around for later innings when things settle down. That's when Wisconsin will really come through with those pay-off blows. Remember, the season isn't over yet. We hope we have a pennant winner for you.

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(Affiliate of International Harvester Company)
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● Better control of quenching temperatures improves the heat-treating process, gives better physical properties to steel, increases production with fewer rejections.

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Write for Bulletin No. 96-MP

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Electron Diffraction of Corrosion Films

(Continued from p. 234)

The second part is concerned with structural factors, including the crystal structure. The third part includes the atomic composition of the film, defects and impurities in the film and the mechanism of reaction. In general, no one technique or method can solve a complicated corrosion problem. The information obtained by electron diffraction is of greatest value when correlated with the results of other studies.

An accurate description of the transmission and reflection methods of electron diffraction is included. Sample preparation, apparatus used and analysis of reflection patterns are given. To obtain a good pattern by the reflection technique the sample must be plane, crystalline and somewhat abraded. Surface preparation is important. During polishing of the sample, care must be taken to prevent contamination of the surface. If it is necessary to study the behavior of the specimens at high temperature, they can be mounted in a furnace and studied in any gas atmosphere and at any temperature of interest. This scheme is especially useful for corrosion studies. The precision obtained in the calculation of the size of a unit cell for cubic structures is of the order of 0.3%.

The dry oxidation of iron was studied, using one or more variables such as time, temperature, pressure, surface preparation and pretreatment. The radii of the diffraction rings and the relative intensities of the lines are used to identify the oxide obtained; the breadth of the lines and the presence of arcs and spots denote the crystal size and orientation. The existence diagram for iron oxide was plotted on a time-temperature chart. The oxides noted were gamma Fe_2O_3 , Fe_3O_4 , alpha Fe_2O_3 and FeO . However, the thickness of the oxides was not determined. In general, thickness is an exponential function of the temperature for a given duration of oxidation and a square-root function of the time at a given temperature.

A complete description of the procedure used in determining the iron system and the results obtained are given in this paper. In general, it was determined from the time-temperature chart that gamma Fe_2O_3 is (Cont. on p. 238)

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GAS . . . OIL . . . OR ELECTRICALLY HEATED

Electron Diffraction of Corrosion Films

(Starts on p. 234) the low-temperature oxide and above 435° F. the oxides Fe_3O_4 and alpha Fe_2O_3 are observed. For long periods of oxidation alpha Fe_2O_3 is formed in the temperature range between 480 and 930° F. For thin films, a transformation is observed between Fe_3O_4 and FeO at a temperature of about 840° F. For thicker films this transformation is observed at about 1020° F., which is in close agreement with equilibrium data for the iron-oxygen system. A similar study of the chromium-oxygen system is also reported.

Transformation was studied during the cooling of two thicknesses of the iron oxide films. There seemed to be a lag in the transformation for a thick film. Cooling experiments in various gas atmospheres showed the importance of studying corrosion reactions under the proper conditions. Different oxides form at a given temperature, depending on the degree of oxidation or reduction. Alloying elements markedly affect the transformations. For instance, FeO is observed at 930° F. on iron, but it does not appear even at 1300° F. on mild steel.

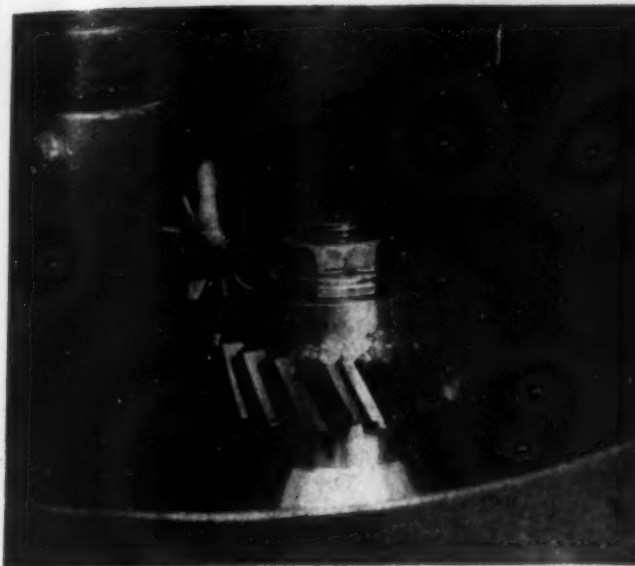
Before electron diffraction is applied to the study of dry oxidation or corrosion, several features should be considered: complexity of the oxides formed, effects of stoichiometric ratio, surface preparation, high temperature, film thickness, and whether or not equilibrium conditions have been attained. A brief discussion of each of these important features is given in the paper.

Life of Ingot Molds*

EXCESSIVE WEAR of ingot molds accounts for 3% of the cost of steel. Molds fail by outside cracks (major cracks) and by erosion on the inside (minor cracks). Major cracks account for the short life of molds; some fail after as few as 30 runs, although the good ones may serve for 300 runs when five-ton ingots are being poured.

(Continued on p. 242)

*Abstracted from "Contributions to the Study of the Life of Ingot Molds", by Robert Stumper. *Revue de Metallurgie*, July-August, 1947, p. 228-233.



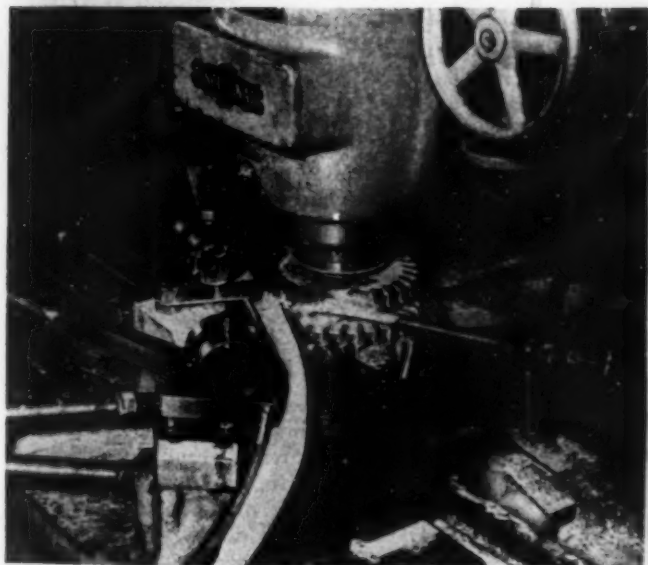
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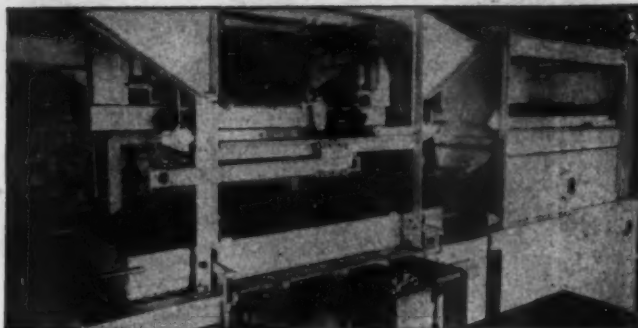
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Transformer Sheet

(Continued from p. 242)

Silicon is needed for two reasons: It produces large, uniform grains and it keeps up to 0.03% C in solution in ferrite. The amount of silicon present above 3.5% is of no value. The action of silicon is strongest at the highest temperature used. Final anneal at 1650° F., instead of at 1560° F., is likely to reduce the hysteresis by 15%.

Aluminum might act in the same manner, but is troublesome, and the real effect of it in transformer iron is in the elimination of oxygen.

The size of ingot seems to be unimportant.

Rapid rolling in the breaking-down operation is helpful. One heating operation is better than two. The material should not be rolled below 1650° F.

Intermediate rolling should be done in at least three or four reheatings, with the final temperature not lower than 1380° F.

Cores in Die Casting*

THE USE of cores in die castings has several advantages, including savings in the weight of the casting, uniform sections, sound castings, a shorter casting cycle as a result of faster cooling, and decreased machining time and cost.

Holes, too small to be cored in a sand casting, can be cored readily in die castings. Occasionally, a threaded core can be used and then even tapping is avoided.

Cores may be fixed or movable, intersecting or collapsible. Large holes and recesses that serve no definite function in the part are produced by cores termed "metal savers". Such cores help keep porosity at a minimum, as well as reduce weight.

The maximum diameter of cores for use with aluminum alloys is about $\frac{3}{8}$ in. and for copper alloys is about $\frac{1}{4}$ in. For zinc and other low-melting alloys, cores down to about 0.040 in. diam. are sometimes used. In general, the draft on cores is preferably not less than $\frac{1}{2}^\circ$ on a side.

The article includes several specific examples of coring, with emphasis on the practical considerations involved in the design of cores.

*Abstracted from "The Importance of Cores in Die-Casting Design", by C. R. Maxon, *Mechanical Engineering*, V. 70, July 1948, p. 609.



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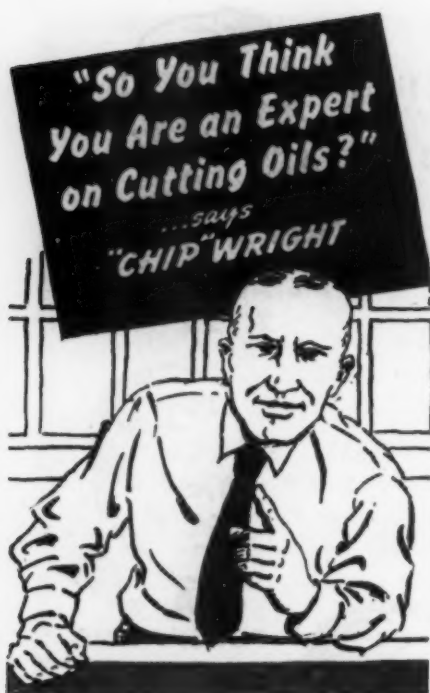
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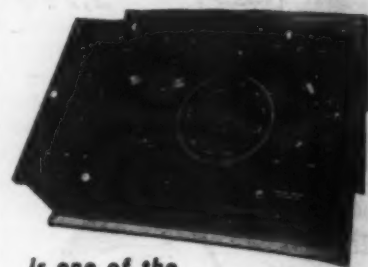
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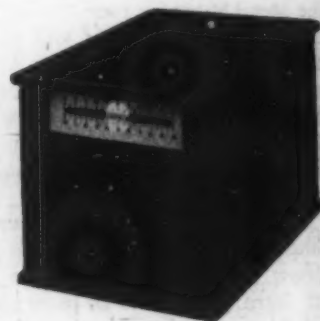
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19-9
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25-20
25-20 Cb
25-20 Mo
25-12
25-12 Cb
18-12 Mo
18-12 MoCb
19-14 Mo
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15-35
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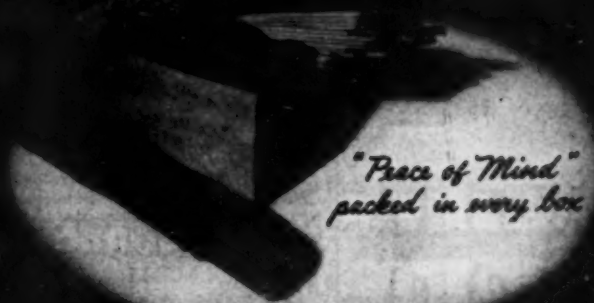
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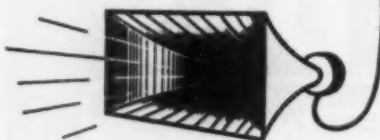
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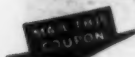


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The wartime scarcity of many nonferrous metals led to the extensive substitution of carbon steel for copper, brass, aluminum, and stainless steel. Although the steel was generally galvanized, zinc tended to form objectionable corrosion products; this brought about a widespread use of chromate films on the zinc, formed by chemical attack in aqueous chromate solutions and, though only a fraction of a mil thick, they helped in inhibiting corrosion. However, as protection apparently was caused by the presence of minute amounts of soluble chromate, slowly liberated by the action of moisture, better corrosion resistance might be obtained by applying a large quantity of chromate to the metal surface. Proteins were good mediums for increasing the amount of chromate since they are basic and readily absorb or combine with chromic acid.

The principal constituents of the chromated protein films are a corrosion inhibitor for the metal, a protein that acts as a vehicle for the inhibitor, a hardening agent, and a bactericide to prevent putrefaction of the protein. The chromate always serves as the inhibitor and may act as the hardening agent and the bactericide as well.

The four functioning constituents of the film can be applied in
(Continued on page 252)

*Abstracted from Technical Report 1208 of the National Bureau of Standards. For further technical details, see "Chromated Protein Films for the Protection of Metals", by Abner Brenner, Grace Riddell and Robert Seegmiller, *Journal of the Electrochemical Society*, March 1948.

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Centrifugal castings are superior castings. The metal is sounder, finer-grained, more uniform. It is free of gas pockets, blow holes and other defects often difficult to keep out of static castings.

Tensile strength is close to that of rolled or hot-forged alloy steel. Dimensions are accurate, usually requiring less machining and finishing and thus speeding production.

If you require extra qualities in your high alloy pipe, investigate DURASPUN Centrifugally Cast Pipe. We can produce it in OD ranging from 2½" to 24" and in lengths up to 15' according to diameter. Our experience in the field of centrifugal high alloy castings dates back to 1931. Our experience in the field of static high alloy casting goes back to 1922. We can give you good service.

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Chromated Protein Protective Films

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a single step or in several steps, according to the compatibility of the agents and the degree of protection desired. In the "two-step" process (usually the most satisfactory) the metal is first dipped into an aqueous protein solution such as gelatin, albumin, or casein. When dry, it is immersed in an acidified chromate solution for ¼ to 3 min. and dried without rinsing. The chromate solution contains chromic acid (¾ to 2%) or a dichromate of zinc, iron, or nickel (1 to 10%).

A simpler "one-step" method, consisting of single immersion in a solution containing both protein and chromate, has the disadvantage that the solution deteriorates slowly. This solution is made by adding ammoniacal zinc chromate to a solution of casein, the resulting mixture containing 10% casein and about 5% zinc chromate.

The chromated protein films are yellow and, unless opaque pigments have been added, are transparent. Their flexibility and adhesion are sufficient to prevent cracking or separation when the metal is bent. They are more effective on large, regular surfaces than on the sharp edges and corners of small objects like nuts and bolts, where the film tends to pull away. Chromated protein films withstand heating to 300° F., whereas most chromate films produced chemically on zinc lose much of their protective value at 212° F. Thickness depends principally on the concentration and viscosity of the protein solutions, varying with the type of protein up to about 0.0002 in.

When freshly prepared and hardened, the films are almost insoluble in water and are so hard that they cannot be scratched with the fingernail. Exposure to light further hardens some films and renders them still less soluble. However, they may be removed quickly from metal parts by an alkaline solution such as 5% sodium hydroxide.

The protein solutions are fairly stable for long periods. Although chromated protein films are superior to direct phosphate or chromate coatings or to oil films for corrosion prevention, they are less protective than suitable paint coatings.

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